R

TRANSFORMATIONS OF TERPENYL OXIRANES BY HETEROGENEOUS CATALYSIS

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CERTIFICATE

This is to certify that this thesis bound herewith is an authentic record of the research work carried out by Mrs. Jayasree.J. under my supervision in partial fulfilment of the requirements for the Degree of Doctor *of Philosophy in* **Chemistry of the University of Kerala and further that no part thereof has been presented before for any other degree.**

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DECLARATION

I, Mrs. Jayasree, J. working under the supervision of Dr. C.S. Narayanan, Head, Food Division, Regional Research Laboratory (CSIR), Thiruvananthapuram - 695 019 do hereby declare that this thesis **"Transformations of terpenyl oxiranes by heterogeneus catalysis"** has not been submitted for the award of any other Degree, Diploma, Title or Recognition before.

Thiruvananthapuram

JAYASREE.J.

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LIST OF SYMBOLS AND ABBREVIATIONS

Å - Angstrum

BE - binding energy

eV - electron volt

g - gram

hr - hour

kHz - kilo hertz

ml - millilitre

mm - millimeter

mmol - millimol

μg - microgram

μl - micro litre

μ sec - micro second

ppm - parts per million

s - surface area

w/w - weight/weight

v/v - volume/volume

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PREFACE

The oxirane ring is one of the most versatile functional group among small rings in organic chemistry. The polarity and strain of the three membered ring allow many reactions with large number of reagents like electrophiles, nucleophiles, acids, bases and radicals. The naturally occurring terpene hydrocarbons can easily be converted to epoxides economically. Some products formed from the isomerization of terpene epoxides are valuable raw materials for perfume, flavourings, cosmetics and pharmaceutical industries, while some products are useful intermediates in organic synthesis.

The present investigation chiefly concerned with the preparation, characterisation and activity determination of aluminium-rare earth binary oxide catalysts like Al_2O_3-Y_2O_3, Al_2O_3-Sm_2O_3, Al_2O_3-Pr_6O_{11}, Al_2O_3-Nd_3O_3 and Al_2O_3-Eu_2O_3. The activity and selectivity of catalysts are studied in the transformation reactions of terpenyl oxiranes like α, β-pinene oxides, (+), (-)-limonene oxides, 3-carene oxide and ar-curcumene oxide.

Varying compositions of Al_2O_3-Y_2O_3 systems are prepared, characterised and activity determined in the transformation of (+)-limonene oxide. Various methods of preparation are adopted for making Al_2O_3-Y_2O_3 (1:1) catalyst and activity and selectivity are determined in the transformation of (+)-limonene oxide. The results of these investigations are presented in this work.

CHAPTER I

HETEROGENEOUS CATALYSIS IN TERPENE CHEMISTRY

1.0 Introduction

Catalytic transformation of petroleum hydrocarbons to useful products over solid catalysts is a well established field in the petroleum and chemical industry. The developments of catalysts to perform specific reactions has also progressed tremendously in the last five decades. There is an abundant resource of chiral organic materials in the form of essential oils composed of terpene compounds. Very useful products for perfumery and pharmaceutical industry could be obtained from terpene hydrocarbons if catalytic transformations were employed. There are very few reports on catalysis of terpene compounds and hence there is a whole field open for active research.

1.1 Heterogeneous Catalytic Systems

Heterogeneous catalytic reactions are by far the most important reactions in man-made chemical conversions. The suitability of catalyst for chemical reactions depend on three factors viz. activity, selectivity and stability. The activity indicates the reactivity of catalytic systems, the rate at which reactants are transformed to products. The selectivity is a measure of the ability of a catalyst to preferentially catalyse one of a number of possible reactions and the stability indicates how long a catalyst will be able to fulfill its action.

The use of heterogeneous catalysts in chemistry provides some advantages over homogeneous catalysts.

1. The separation of the catalyst from reaction mixture is easy
2. Repeated use of the catalyst is possible and
3. High activity and selectivity of the catalysts.

The use of solid acid-base catalysts have some advantages over traditional acid-base catalysts. These catalysts are easily disposable and produce no corrosion to the system. Moreover, some solid catalysts exhibit acid-base bifunctional nature. Depending on the surface properties, solid catalysts are divided mainly into three groups. Solid acids, solid bases and solid acid-base bifunctional catalysts.

There are excellent reviews on the characterisation of acidic and basic properties of solid catalysts[1,2]. Tanabe has contributed extensively on solid acids and bases[3,4,5]. There are a number of methods employed for determination of surface acidity and basicity. Each of them taken by itself give some useful informations, but none of them give a complete picture of surface acid-base properties of the solid under examination. A very brief review of the acidic and basic properties of oxide catalysts along with their determination is attempted.

1.2 Solid Acid Catalysts

The concept of surface acidity was orginally introduced with the aim of explaining the presence of some products formed in catalytic chemical reactions, not as a consequence of suppositions about the nature of surface-active sites of solid catalysts. Acid properties on a solid surface requires the description of acid strength, acid amount and their nature whether they are Bronsted or Lewis type. Acid strength and acid amount are strictly inter connected and most of the experimental methods can give a measure of total acidity of both types.

1.2.1 Acid strength

The acid strength of a solid is the ability of the surface to convert an adsorbed neutral base in to its conjugate acid[6]. If the reaction takes place through the transfer of a proton from the solid surface to the adsorbed molecule (Bronsted acidity) or of an electron pair from the adsorbed molecule to the solid surface (Lewis acidity), the acid strength can be expressed, respectively, by means of the Hammett acidity function Ho as follows[7,8,9].

$$Ho = pKa + \log[[B]/[BH^+]] \longrightarrow \quad (1)$$

or

$$Ho = pKa + \log\,[[B]/[AB]] \longrightarrow \quad (2)$$

where Ka is the equilibrium constant of the dissociation of the acid and [B], $[BH^+]$ and [AB] are the concentrations of neutral base, its conjugate acid, and the addition product formed during the adsorption of the base on the Lewis centre respectively.

Colors of adsorbed Hammett indicators can be used to bracket the Ho of a solid surface in the same way that the colors of more conventional acid-base indicators are used to bracket the pH of an aqueous solution. When an acid color is obtained for the adsorbed indicator, the Ho of the solid surface is equal to or lower than the pKa of the indicator.

Color tests were made by adding 3-5 ml of dry benzene to 100 mg of dried, powdered solid, adding a few drops of a 0.1% solution of indicator in benzene, mixing the resulting suspension and noting the color developed on the catalyst surface.

1.2.2 Acid amount

The amount of acid sites on a solid is usually expressed as the number of m mol of acid sites per unit weight or per unit surface area of the solid. The determination of the number of acid sites in which the solid suspended in non-aqueous solvent, is titrated with n-$BuNH_2$, using an adsorbed Hammett indicator to establish the end point. This method was developed by Johnson[10]. The result will be only for sites whose acid strength is greater than or equal to that of indicator used. Benesi has further developed this method, using a series of indicators, to get a distribution of acid sites of varying strength[11].

The acidity values obtained from a series of indicators are cumulative from the least basic indicator to the most basic one. Hence this method gives an idea of the heterogenecity of the surface. However, Hammett indicators are unable to distinguish between Bronsted and Lewis acids. Hirschler developed more proton specific aryl methanol indicators[12] which react with Bronsted acids according to the equation

$$ROH + H^+ \longrightarrow R^+ + H_2O \longrightarrow \qquad (3)$$

where R^+ is a colored carbonium ion. A new acidity function, denoted by H_R by Deno[13] was used to define acid strength in terms of these aryl carbinol indicators and given by equation (4) as follows.

$$H_R = -\log aH^+ + \log {}^aH_2O + \log (fR^+/fROH) \longrightarrow (4)$$

and hence the two surface acidity functions are related by equation (5) as follows

$$H_R = Ho + \log {}^aH_2O - \log \left(\frac{fROH \cdot fBH^+}{fB.fR^+}\right) \longrightarrow \qquad (5)$$

In the case of visible indicators, physical adsorption of indicators on the surface of the catalyst, may cause a spectral shift to longer wave lengths which cause over estimation of the number of acid sites of specific strength. Such errors can be avoided by fluorescent indicators which are colored in both acidic and basic forms and can be used more accurately for the visible determination of end point. This ultimate technique for the non aqueous titration of surface acidity was developed by Drushel and Sommers[14] who employed spectrophotometric measurements of adsorbed indicators to determine end points. Ultraviolet indicators listed in Table-1 are used if the end point is determined spectrophotometrically[14].

Optical spectroscopy provides a method which can be applied for the quantitative and qualitative determination of acid centers as well as for their determination of individual nature (Bronsted or Lewis type)[15,16,17]. Ammonia or pyridine can be used for IR studies of chemisorbed bases. From the adsorption bands a direct evidence for the existence of Bronsted and Lewis sites can be obtained[18,19]. A list of commonly used solid acids are given in Table-2.

1.2.3 Some Solid Acids

1.2.3.1 Alumina

Alumina is most widely used as a catalyst or catalyst support. It's robust, porous and inexpensive nature make it a support or co-catalyst in the process of industrial importance like isomerization, alkylation, catalytic cracking and hydroforming[20-26]. Most important

Table 1

Basic Indicators for Spectrophotometric Determination of Acid Strength

Indicator	pKa
Phenyl azonaphtyl amine	+4.0
P-Dimethyl aminoazo benzene	+3.3
Amino azobenzene	+2.8
Benzene azodiphenyl amine	+1.5
P-Nitro aniline	+1.1
O-Nitro aniline	-0.2
P-Nitrodiphenyl amine	-2.4
2,4-Dichloro-6-nitro aniline	-3.2
P-Nitroazo benzene	-3.3
2,4-Dinitro aniline	-4.4
Benzal acetophenone	-5.6
P-Benzoyl diphenyl	-6.2
Anthraquinone	-8.1
2,4,6-Trinitroaniline	-9.3
3-Chloro-2,4,6 - trinitro aniline	-9.7
P-Nitrotoluene	-10.5
Nitrobenzene	-11.4
2,4-Dinitrotoluene	-12.8

thing is that alumina can be 'tailored' to suit the requirements of diverse catalytic reactions.

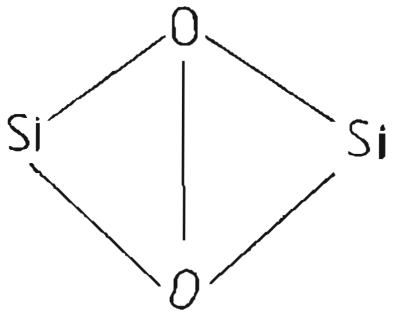
Aluminas having varying surface areas can be prepared by thermal decomposition of its hydroxides or by precipitation as colloidal gels. The colloidal gels are often preferred as supports in commercial reforming and hydrotreating catalysts because they can be prepared in a pure state and their porosities and surface areas are readily adjusted by appropraite choice of gelation conditions. The surface of uncalcined aluminas consists of amphoteric hydroxyl groups which are feebly acidic, unless they have acid producing impurities. When aluminas are activated above 500°C, a variety of surface groups are formed[16,27]. Primary change on heating is the removal of most of the hydroxyl groups, but some remain even at high temperatures of 800-1000°C[28].

During heating several types of oxide ions are produced on the surface of alumina by condensation of hydroxyl ions[29] and these oxide rich portions of alumina surface contain incompletely coordinated aluminium ions that are centers of Lewis acids[19,30]. The acid strength of these centers increase with the number of oxide ions.

Aluminas are capable of skeletal isomerization of olefins[31,32], double bond isomerization[30-32] etc. However the complexity of each reaction depends on the model reaction studied. Indicator tests showed that the seat of activity in γ-alumina as Lewis centres[32,35]. *Infra red study of pyridine* chemisorbed on alumina verified the existence of Lewis acidity and the absence of Bronsted acidity[19,34]. Acidity on the surface of alumina can be promoted by addition of other anions like fluoride, phosphate, BF_3 as well as other metal oxides[3,35,36].

1.2.3.2 Silica gel

Pure silica gel is inactive for demanding acid-catalyzed reactions, evidently because surface SiOH groups have only feeble acid strength. The pKa values of such groups fall somewhere in the range of 4 to 7 *depending on* the type of measurement[37-39]. Infra red studies of bases chemisorbed on silica gel also show that the SiOH groups are only weakly acidic. When silica gel is heated at 500°C or above, most of the surface SiOH groups are removed[40]. Morrow and Cody[41] suggested the formation of reactive sites on silica gel by dehydroxylation and they found the presence of strained si-o-si bridges as reactive sites. Low and Morterra[42,43] showed that a reactive form of silica gel can be prepared by a three step process consisting of methoxylation of silica gel, pyrolysis of the product, and removal of surface SiOH groups. They postulated that the reactive sites are made of biradical centers.



Although pure silica gel is catalytically inactive for skeletal transformations of hydrocarbons, only trace amounts of acid-producing impurities like alumina provide catalytic activity. Tamele et al.[44] showed that introduction of little amount of aluminium in silica gel made a 40 fold increase in cumene conversion at 500°C.

Surface acidity and catalytic activity of silica can be generated when non metal or halogens interacted with silica gel[45]. Phosphoric acid mounted on silica gel is active for hydrocarbon cracking.

1.3 Rare Earth Oxides

The history of rare earth elements begin in 1788 in Sweden with the discovery of ytterbite by Arrhenius. The systematic study of rare earth's separation properties began in 1940. From that time they are used for various research programmes in industrialised countries. Rapidly rising applications of rare earths started from 1960.

The special combination of inherent physical and chemical properties of the lanthanides sets them apart from all other elements. The lanthanides are a group of fairly electropositive elements and their 4f electrons do not have a significant radial extension beyond the filled $5s^2 5p^6$ orbitals of the xenon inert gas core. The lanthanides therefore appear like closed shell inert gas with tri positive charge. The most stable alternate oxidation states are formed by elements that can attain empty, half-filled or filled f levels. This property of rare earths is widely utilized as oxidants in orgnic chemistry[46-52]. Owing to lanthanide contraction, higher coordination numbers are most common in higher lanthanides.

The chemical and ceramic properties of rare earth elements result from their high affinity for oxygen producing highly stable oxides which can be used in high temperature materials. Y_2O_3 help in the stabilization of ZrO_2, which serves as an electrode.

Chemical properties of rare earth elements are used in the largest field of application as catalysts. Most important are the cracking catalysts for the petroleum industry. The rare earth elements combined into molecular sieves serve in fluid bed or fixed bed reactors to increase the yield of gasoline. In addition, there are the combustion catalysts for automobiles for air pollution ntrol. The rare earth elements are physiologically inert d therefore present no danger to the environment. One of e largest single use for rare earth mixtures is in fluid acking catalysts in petroleum industry[53]. All zeolite acking catalysts currently manufactured contain rare earth ides present as a mixture of the rare earth elements since olite catalysts containing rare earth are structurally re stable and maintain their hydrogen transfer properties.

Since 1962 rare earths have been used to stabilize lite cracking catalysts for the petroleum industry[54]. il recently this application to catalysis has been the y commercially significant one. Currently however, a ber of new applications of potential commercial nificance are appearing. One of the most important of se is the use of cerium in catalysis for automobile aust emission control. The rare earth oxides have a ber of distinguishing properties important in catalytic lications. The oxides are basic[55] compared to alumina, thanum oxide being most basic. The oxides also have good rmal stability, a valuable characteristic in most ustrial applications. Cost and abundance are important perties to be considered for any commercial application. ortant potential catalytic applications include, ammonia thesis, hydrogenation/ dehydrogenation, polymerisation, merization, oxidation, auto exhaust emission control etc.

Oxides like La_2O_3, Y_2O_3, Sm_2O_3, Gd_2O_3 or Dy_2O_3 were used for catalytic combustion[56], for stabilizing alumina[57] and other metallic oxides like MgO, SiO_2, MnO and Fe_3O_4[58]. For isomerization of various menthadienes[59] these oxides are used. Rare earth oxides were also used for the hydrogenation of olefins[60] in the isomerization of butenes[58,5,61,62] and for the oxidative coupling of methane[59]. La_2O_3, ThO_2 are widely used for the hydrogenation and dehydrogenation of 4-isopropenyl-1-methyl-cyclohexane[56]. The catalytic behaviour of lanthanide/SiO_2 catalysts varied with levels of lanthanide loading which is used for hydrogenation of alkyne[63].

1.4 Solid Base Catalysts

Base strength of a solid surface is defined as its proton accepting ability and is expressed by Hammett and Deyrup H_- function[64a] after the analogy of acid strength by Ho function.

$$BH = B^- + H^+ \longrightarrow (6)$$

$$H_- = -\log aH^+ + fB^-/fBH$$

$$= pKBH - \log C_{BH}/C_B^- \longrightarrow (7)$$

where aH^+ is the activity of the proton adsorbed on the surface and f and c are the activity coefficient and the concentration of an adsorbed indicator. As evident from equation (7), base strength of solid surfaces increase with an increase in H_-. Base strength of a variety of basic solids were measured from the color changes of a series of H_- indicators adsorbed on the solids. Base strength distribution of solids were measured by titration of materials suspended in benzene with benzoic acid[64b] or CO_2[3].

The alkaline earth oxides like CaO show maximum basicity when calcined at 500°C[61] and the number of reducing sites increased upto 700°C. Strong basic sites are surface O^{2-} and weaker ones are surface OH groups. Surface dislocations act as reducing sites[61]. Since water is amphoteric and carbon dioxide is acidic, fresh basic oxides may adsorb them from atmosphere, forming surface hydroxides and carbonates. The heat treatment of such solid bases result in a progressive elimination of adsorbed water and CO_2. This elimination involves the reappearance of basic sites with an inherent base strength of the solid. Further evidence for the extent of such poisoning is provided by the fact that, the difference in base strength between an untreated solid and the evacuated appear to increase with an increase in base strength of solid-base surfaces.

Relative basic strength of alkaline earth oxide is $BaO > SrO > CaO > MgO$[62] and order of basicities in m mol/g is $MgO > CaO > SrO > BaO$[62]. Y_2O_3, La_2O_3 and CeO_2 are less basic than alkaline earth oxides[63], but more basic than ZrO_2

and ThO_2[64a]. A list of commonly used solid base catalysts are given in Table 3. Generally the oxides of the upper part of the periodic table has higher acid strength and lower basic strength as compared with that of lower part in the same group and the oxide of the metal of the left side in the periodic table has higher basic strength and lower Lewis acid strength as compared with that of the right side in the same period. If the crystal structure of two oxides were same then the electronegativity of the metals govern their acid-base property.

Table 3

List of Commonly used Solid Base Catalysts

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1. Mounted bases NaOH, KOH on silica, alumina alk. metal and alk. earth metal dispersed on silica, alumina, carbon.
2. Anion Exchange resins
3. Charcoal heat treated at $1173^{o}K$ or activated with N_2O, NH_3 or $ZnCl_2$ - NH_4Cl-CO_2
4. Metal oxides :

   BeO, MgO, SrO, CaO, Al_2O_3, Y_2O_3, La_2O_3, CeO_2, ThO_2, TiO_2, ZrO_2.
5. Metal salts

   Na_2CO_3, K_2CO_3, $KHCO_3$, $CaCO_3$, $SrCO_3$, KCN
6. Mixed oxides:

   SiO_2 - MgO, SiO_2 - CaO, SiO_2 - WO_3, SiO_2 - SrO, Al_2O_3 - MgO, Al_2O_3 - ThO_2, Al_2O_3 - ZrO_2, MgO - TiO_2.

1.5 Solid Acid-Base Catalysts

Solid acids have a basic property and solid bases have an acidic property also. So the classification of solid acids and bases is made by their predominent property. A solid acid-base catalyst may be defined as a solid catalyst possessing both acidic and basic properties which play important roles for catalytic action. Oxides like ZrO_2,ThO_2 and ZnO act as weak solid acid base catalysts[65-67]. Alumina has Lewis acidity, but it shows basicity when small amount of water or impurities were present on its surface[68]. A mixture of TiO_2 and MgO or TiO_2-ZrO_2 show acid base property[69].

1.6 Orgin of Acidity

Tanabe have proposed a hypothesis that acid sites on binary metal oxides are formed by an excess of a negative or positive charge in the mixed oxides[70]. The charge whether excess or not and positive or negative are determined by the coordination numbers and valencies of the positive and negative elements.

The hypothesis is based on two postulates. (1) The coordination number of a positive element of a metal oxide and that of a second metal oxide are maintained even when they are mixed. (2) The coordination number of a negative element (oxygen) of a major component oxide is retained for all oxygens in a binary oxide. As an example the structure of TiO_2 - SiO_2 where TiO_2 is the major component oxide, and SiO_2-TiO_2 where SiO_2 is the major oxide are given in figures (1) and (2).

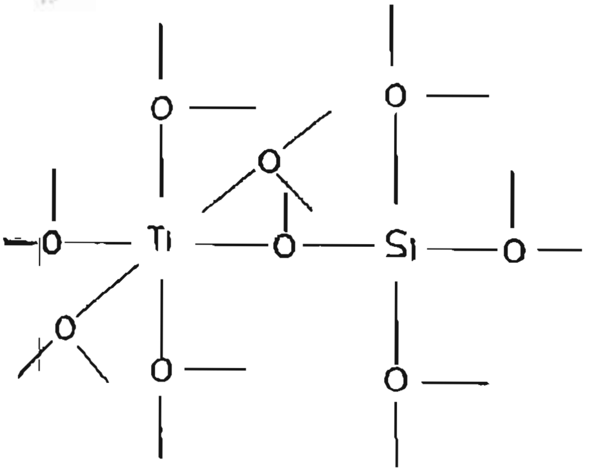


Fig. 1

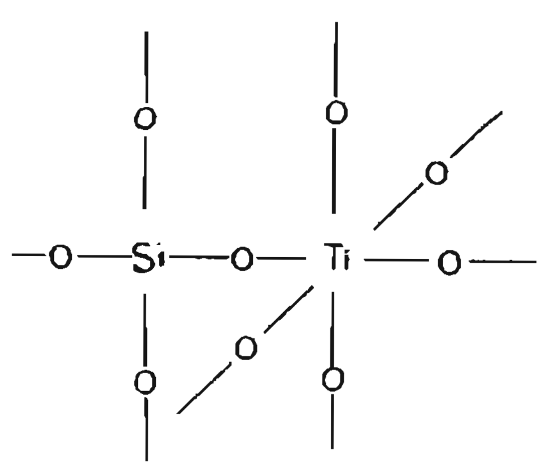


Fig.2

In Figs. (1) and (2), the coordination numbers of positive elements in the component single oxides remain 4 for Si and 6 for Ti when they are mixed, where as those of the negative elements should be 3 and 2 respectively. In Fig. 1 the four positive charges of Si atom are distributed to four bonds ie., a positive charge is distributed to each bond, while the two negative charges of oxygen atom are distributed to three bonds, ie., -2/3 of a valence unit is distributed to each bond. The difference in charge for one bond is +1-2/3 = +1/3, and for all the bonds the valence unit of +1/3 x 4 = +4/3 is excess. In this case, the Lewis acidity is assumed to appear on the presence of an excess of the positive charge. In Fig. 2 the four positive charges of the titanium atom are distributed to six bonds, ie., +4/6 of a valence unit to each bond. The charge difference for each bond is +4/6-1 = -1/3, and for all the bonds the valence unit of -1/3 x 6 = -2 is excess. In this case, Bronsted acidity is assumed to appear because two protons are considered to associate with six oxygens to keep the electric neutrality. In any case, TiO_2-SiO_2 is expected to show an acidic property because of the excess of a positive or negative charge.

The present hypothesis predicts which combinations of oxides in the periodic table will generate acidity and at what compositions the Bronsted or Lewis acidity will appear, but it does not predict the acid strength of the oxide mixture. The postulates of the hypothesis are applicable only to chemically mixed binary oxides and not for mechanical mixtures. Tanabe has made another study of metal oxides prepared by coprecipitation method, and correlated their acid strength with average electronegativities of metal ions[71]. They observed that highest acid strength were found to increase with increase of the algebraically averaged electronegativities.

Thomas proposed[72] that the acidities of binary oxides are generated when $c_1 = c_2$ and $v_1 < v_2$ or when $c_1 = 2c_2$ where c_1 and c_2 are the coordination numbers of a positive element and a second one, where v_1 and v_2 are the valencies of the respective positive elements.

Tanabe's mechanism based on excess charges on the surface of oxides leading to acidity have superiority over other proposed theories, since their studies revealed a 90% validity of the hypothesis.

1.7 Orgin of Basicity

On an oxide surface, a combined oxygen atom in an oxide surface can act as an electron donor and its capacity is expected to be related to the effective negative charge on the oxygen atom[73]. The higher the negative charge, the stronger the base property. Sanderson[73] suggested that the partial negative charge on a combined oxygen anion has been estimated from the electro negativity equalization principle. According to this theory the base strength of alkaline earth oxides is expected to decrease in the order of SrO, CaO and MgO. A good agreement in the order of base strength between the observed and expected strongly suggests that the combined oxygen anion acts really as a basic site on the oxide surfaces.

If the surface of a basic oxide has a regular structure, the base strength would be uniform. In actual cases the basic oxides have irregular surface structures possessing many kinds of defects, which would be produced more easily in oxides of high melting points than in those of low melting points. Some surface hydroxyls will be present on defect sites also. Combined oxygen anions in

In the next decade several concepts were propounded. Taylor[77] advanced reasons why preferential adsorption takes place on active centers and why these centers have highest catalytic activity. At this time Balandin proposed his multiplet hypothesis[78-81]. The multiplet theory proceeds from the premise that catalysis is a chemical phenomena, and that covalent bond require catalytic activation. The energy of the chemical valence interaction of two atoms A and B bound together with covalent bonds is characterised by a potential curve, presenting the energy as a function of distance between the centers of the atoms.

According to this theory, the molecule as a whole do not take part in catalytic reaction but single atoms belonging to them come in contact with each other on the surface of catalyst. A group of surface atoms attract reacting molecule and that is referred as multiplet.

By 1940 the theory of absolute reaction rates, the suggestion that for metallic and semiconductor catalysts, forces other than chemical interaction between surfaces and adsorbed species were responsible for their action. Now band theory, ligand field theory can be applied for describing the overall electron concentration of the solid.

One of the main features displayed by a heterogeneous catalyst is an enhancement in reaction rate of a given process by virtue of a diminution in the activation energy. This is inextricably bound up with the adsorption energy of the activated complex. The stronger the adsorption, the lower the activation energy for adsorption, but now a higher activation energy is required for the desorption of products. On a certain part of the surface only, the respective activation energies will have their optimum values. Thus the energy of adsorption of the activated complex on an optimum site will be sufficiently large to allow surface reaction to occur and yet not be too great to impede the desorption of products.

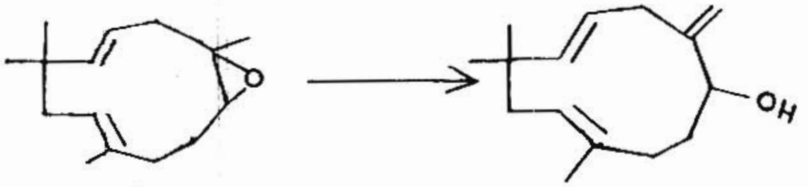
1.9 Rearrangements of Terpenes and Terpenyl Oxiranes over Solid Acid-Base Catalysts

1.9.1 Rearrangements of Terpenyl Oxiranes

The oxirane ring is one of the most versatile functional group among small rings in organic chemistry. The polarity and strain of the three-membered ring allow many reactions with large number of reagents like electrophiles, nucleophiles, acids, bases and radicals. The naturally occuring terpene hydrocarbons can easily be converted to epoxides economically. Some, products formed from the isomerization of terpene epoxides are valuable raw materials for perfume, flavourings, cosmetics and pharmaceutical industries. While some products are useful intermediates in organic synthesis.

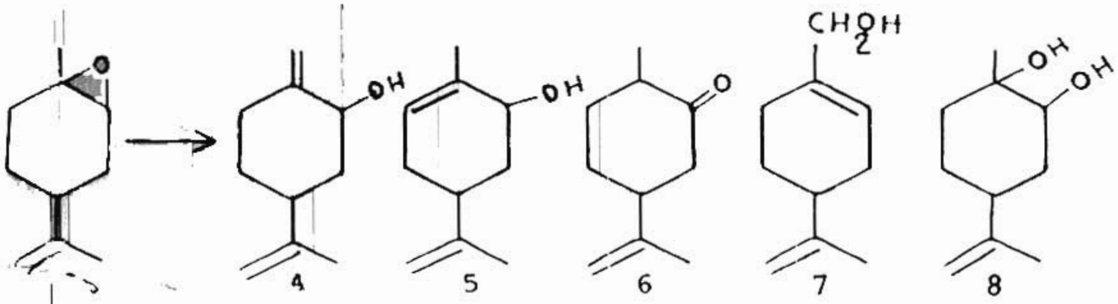
Several workers have studied the isomerizations of limonene, carene and pinene oxides catalyzed by Al_2O_3 and SiO_2. The first isomerization work was performed by Humbert and Guth[82], where the reaction of limonene oxide was carried out in the presence of alumina at 200°C.

Alumina and silica gel are industrially important in catalytic processes, especially in petrochemical industry. In laboratory these materials are put to use as adsorbents in the chromatographic separation of compounds. It was during such an application the interesting reaction of isomerization was observed[83]. When humulene epoxide was chromatographed on active Al_2O_3, much of the epoxide was lost by conversion to alcohols[84].

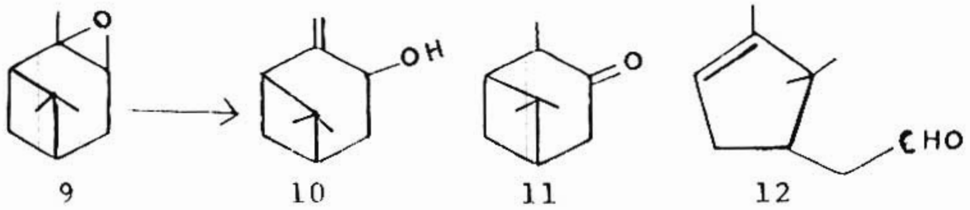


1 2

When Nigam and Levi[85] chromatographed limonene oxide on active alumina, it isomerized yielding mainly corresponding, α,β-unsaturated alcohols, exocarveol (4) and endocarveol (5) with some products like dihydrocarvone (6), perillyl alcohol (7) and 8,(9)-p-menthene 1,2-diol (8). The product distribution changed with nature of alumina, whether it is basic, neutral or acidic.

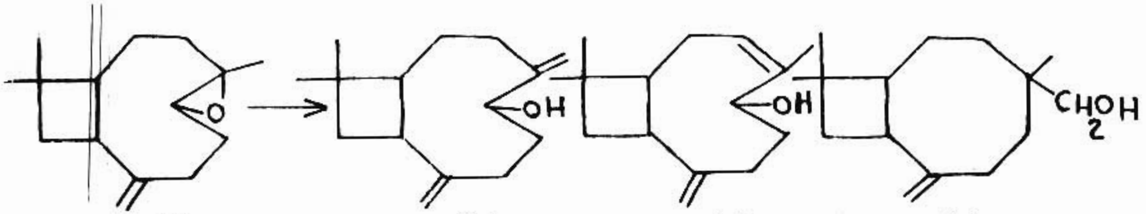


When chromatographed on alumina[86], α-pinene oxide (9) isomerized to give pinocarveol (10) cis and trans pinocamphone (11) and α-campholenic aldehyde (12). Nature of the products largely depend on the nature of alumina employed.



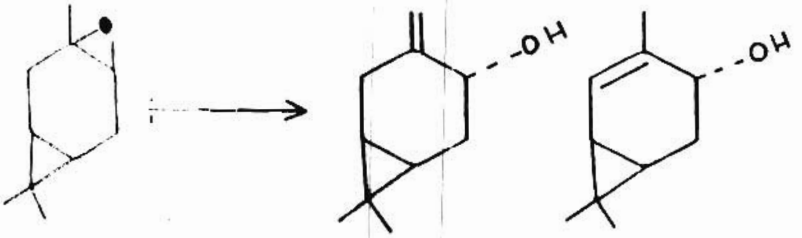
In this reaction 92% selectivity for the formation of pinocarveol was observed over Al_2O_3 treated with KOH and NaOH while 84% selectivity for pinocamphone over Al_2O_3 doped with $LiClO_4$.

Several group of workers started studying the isomerizations of limonene, carene, pinene and other epoxides over Al_2O_3, silica and other metallic oxides. Tanabe and co-workers were prominent among them. They studied the isomerization of caryophyllene oxide[69] on active Al_2O_3, in petroleum ether to give three alcohols (14,15,16)



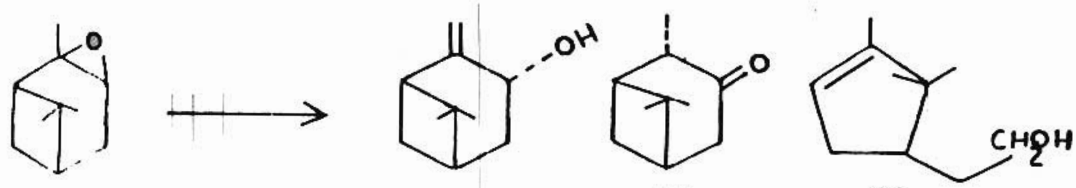
13 14 15 16

Sukh Dev and his co-workers studied a number of rearrangement reactions over alumina and silica gel. 3-carene oxide (17) in hexane rearranged to give two isomeric alcohols[87], trans-3(10)-caren-4-01 (18) and trans-2-caren-4-01 (19)



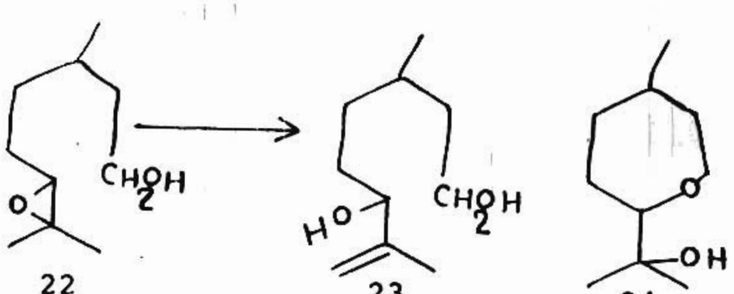
17 18 19

Similarly the isomerizations of epoxy pinene β-himachalene oxide and β-citronellol oxide were carried out. Epoxy pinene[88] was converted to trans-pinocarveol (20) pinocamphone (11) and α-campholenic alcohol.



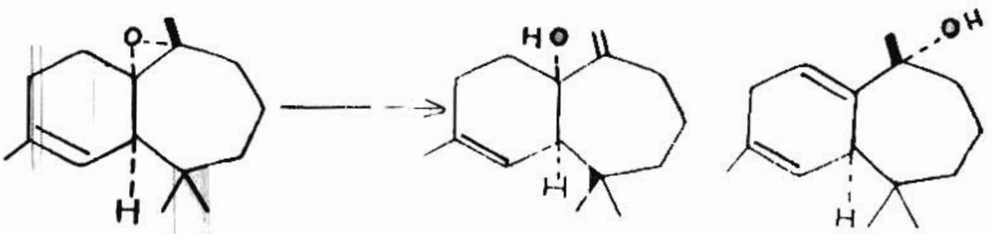
9 20 11 21

β-citronellol oxide (22) isomerized to 6-hydroxyl (3,7-dimethyl) oct-7-en-1-01 (23) and 5-methyl-2-(2) hydroxy isopropyl) oxepane (24) over Al$_2$O$_3$[87].



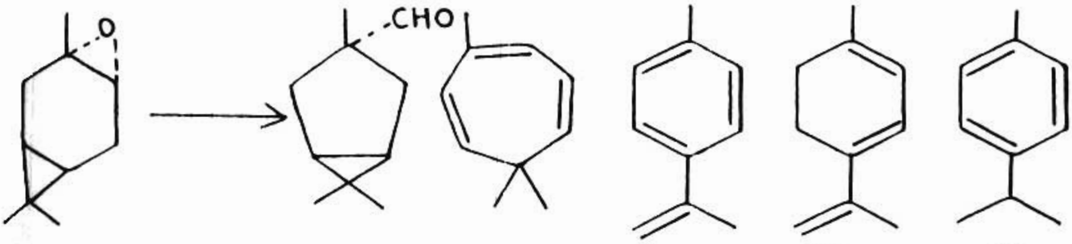
22 23 24

β-Himachalene oxide (25) gave mainly allylic alcohols of 6α-hydroxy-1α-himachala-2,7(14)-diene(26) and 7α-hydroxy-1α-himachala-2,5-diene (27) over Al$_2$O$_3$.



25 26 27

Carene oxide (17) rearranges to 3,6,6 - trimethyl bicyclo [3.1.0] hexane-3-carbaldehyde (28) and some other hydrocarbons[89] like 3,7,7 - trimethyl tropilidene (29), 1-methyl-4-isopropenyl-benzene (30), 1,5,8(9)-p-menthatriene (31), and p-cymene (32).

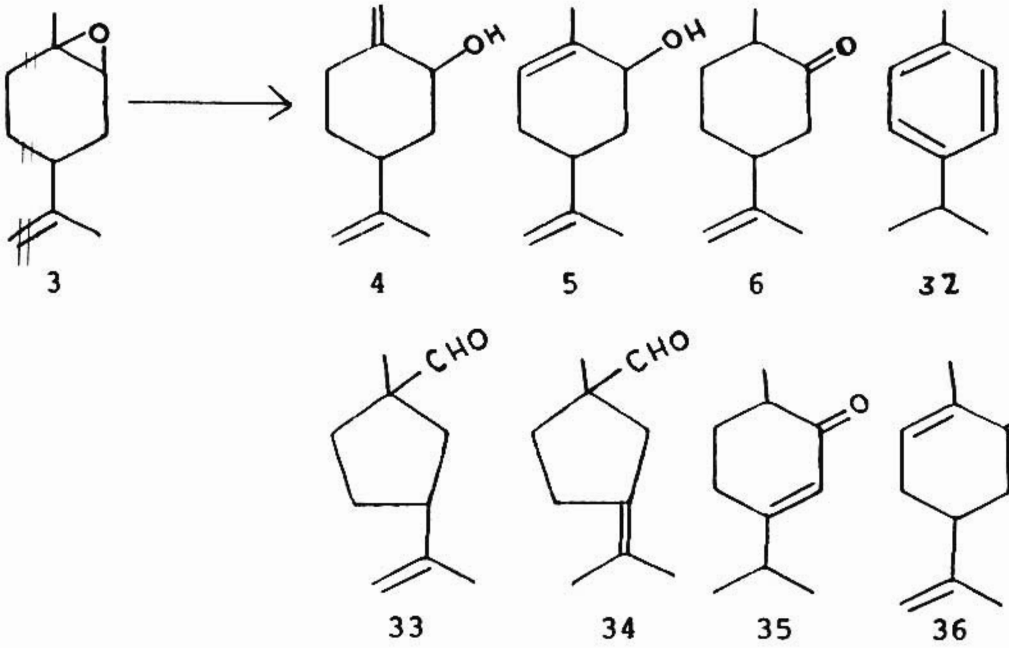


17 28 29 30 31 32

In this reaction composition of the product was dependent on the silica gel-substrate ratio.

Joshi and co-workers [90] found that the reactions of carene oxide and other epoxides over active Al_2O_3, four different types of reactions were observed (1) transformation to allylic alcohol (2) hydration to a trans-glycol (3) isomerization to a ketone (4) carbonium ion rearrangements. These workers pictured the transformations as the coordination of epoxy oxygen with an electron acceptor site on catalyst surface, with oxirane ring clevage and simultaneous proton elimination in the case of allyl alcohols.

In 1970s the first systematic isomerization reaction in a heterogeneous system was investigated by Arata and Tanabe[91,92,93]. d-Limonene oxide was isomerized in toluene at 108°C to p-cymene (32), 1-methyl-3-isopropenyl cyclopentane-1-carbaldehyde (33), 1-methyl-3-isopropylidine cyclopentane-1-carbaldehyde (34), carvenone (35), carvone (36) cis and trans - dihydrocarvone (6) cis and trans-exo carveol (4) and cis and trans - endo carveol (5).



3 4 5 6 32

33 34 35 36

Tanabe and co-workers investigated this reaction using various solid acids, bases, acid-bases, mounted acids and over compounds like BF_3-etherate, $LiClO_4$. The total yield and percentage of products varied largely with type of catalyst used. Acidic catalysts like SiO_2-Al_2O_3, BF_3

etherate and $LiClO_4$ formed carbonyl compounds in greater yields (at least 80%). Solid H_3PO_4 heat-treated at a low temperature gave comparatively uniform yields of all the compounds, though ketone was relatively predominent. The time variation of the products over SiO_2-Al_2O_3 suggests the preferential isomerization of the cis form to 35 and 33 to 34. The isomerization occurs to form a compound containing exodouble bond in a 5-membered ring and one with endo double bond in a 6-membered ring. These are due to their stabilities[94,95].

From the product distribution over catalysts like solid H_3PO_4, H_2SO_4/SiO_2 and SiO_2-Al_2O_3 the double bond migration is considered to be catalyzed by Bronsted acids[96]. The formation of a very large amount of carvenone (35) over H_2So_4/SiO_2 leads to this conclusion. In a homogeneous catalytic reaction with CH_3COOH-1% H_2SO_4 at 16°C for 8hr, limonene oxide rearranged into 35% carvenone (35), 16% dihydrocarvone (6) and 10% cymene[96]. The cymene formation is also interpreted as Bronsted acid-catalyzed dehydration of the reactant with a subsequent shift of double bond of the isopropenyl group to the 6-membered ring. BF_3, a typical Lewis acid showed high selectivity for the formation of ketones. Other Lewis acids $ZnCl_2$, $ZnBr_2$ showed similar reactivity[96,97].

MgO and CaO have no basic strength enough to bring about the transformation of epoxides[98]. The isomerization of d-limonene oxide was studied over $NiSO_4$ and $FeSO_4$ calcined at various temperatures[92]. Compounds p-cymene, 1-methyl 3-isopropylidine cyclopentane-1-carbaldehyde, carvenone were slightly produced over these catalysts, contrast to the large quantities of these materials over solid H_3PO_4, H_2SO_4/SiO_2 and SiO_2-Al_2O_3. Since these catalysts are free of strong Bronsted acid sites whose acid strength is high enough to bring about isomerizations of double bond of the isopropenyl group or dehydration of the reactant. Catalytic reactions of metal oxides largely depend on preparation and pretreatment conditions of catalyst. Dihydrocarvone was formed over $FeSO_4$, while exo and endo allyl alcohols were predominently formed over TiO_2, TiO_2-ZrO_2 and ZrO_2. $NiSO_4$ produced approximately the same quantity of both ketone and allyl alcohols. Compound 1-methyl, 3-isopropenyl cyclopentane-1-carbaldehyde was largely formed over $NiSO_4$ when calcined at low temperature and $FeSO_4$ when calcined at high temperature.

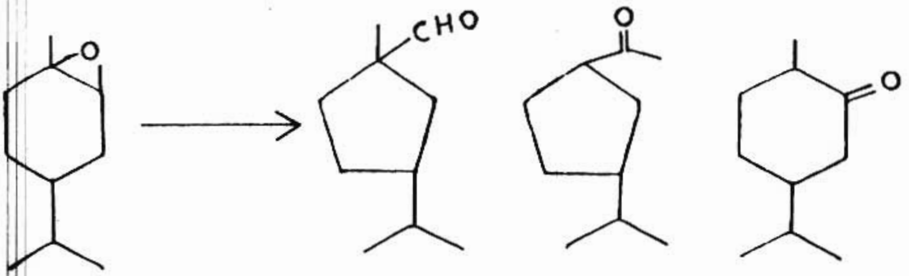
Over $NiSO_4$ catalyst which was calcined at 250°C trans forms of dihydrocarvone, exo-and endo-allyl alcohols diminished greatly after 25 min, while those of the cis form increased after 25 minutes. Similar observations were made over $FeSO_4$ and TiO_2-ZrO_2 for trans forms of allyl alcohols.

In the formation of allyl alcohol, exo-alcohol was predominently formed over endo-alcohols over $NiSO_4$, TiO_2 and TiO_2-ZrO_2 while ZrO_2 give preference to endo-alcohol formation. The preferential formation of exo-alcohol is due to abstraction of primary proton over secondary one. This is due to the enhanced acidity of primary hydrogen due to electronic effect[98,99]. Steric factors also play a role as the abstraction of a proton on a carbon atom outside the ring is easier than that of a proton on the ring.

Allyl alcohols largely formed on TiO_2-ZrO_2 explains the bifunctional nature of the catalyst. The choice of the endo-or exo-double bond formation depend on the distance between acidic and basic sites on the catalyst. The bifunctional mechanism was experimentally proved by using the deuterated epoxide, 1,2 epoxy cyclohexane 3,3,6,6-d_4[100]. From isotopic studies it was concluded that the expoxide is adsorbed on a pair of acidic and basic sites, and that allyl alcohol is formed when both the opening of the epoxide ring and the hydrogen abstraction are simultaneous, while ketone is formed when the former is prior to the latter.

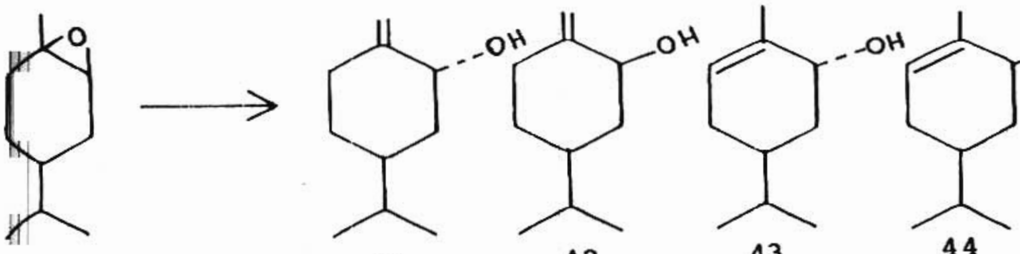
[illegible] when used for isomerization of d-limonene oxide behaved differently depending on different preparation conditions. Al_2O_3 prepared by hydrolyis of its sulphate and various commercial samples were used for the study. Al_2O_3 sample prepared by hydrolysis produced carbonyl compounds and allyl alcohols in equal amounts while one commercial sample produced more carbonyl compounds and another sample produced more allyl alcohols. The allyl alcohols produced were of trans form.

Settine and his co-workers found that carvomenthene epoxide (37) in the presence of $ZnBr_2$ rearranges with ring contraction to 1-methyl-3-isopropyl cyclopentane-1-carbaldehyde (38) and methyl (3-isopropyl-cyclopentyl) ketone (39) and carvomenthone[98] (40).



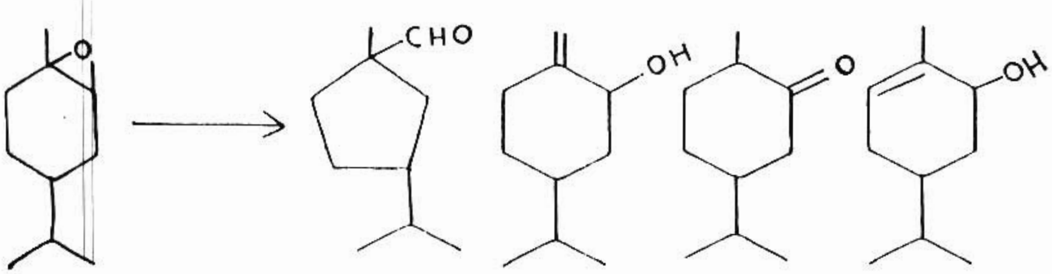
37 38 39 40

Eschinasi reported the rearrangement of this epoxide presence of aluminium isopropoxide (in small amounts) to ylic alcohols[97], 1,(7)-p-menthen-2-01 (41,42) and rvotanacetol (43,44) in high yields.



37 41 42 43 44

Arata and coworkers studied the isomerization of carvomenthene oxide in heterogeneous conditions as in the case of d-limonene oxide[101] over various solid acid base catalysts. The products they obtained were 1-methyl-3-isopropyl cyclopentane - 1 - carbaldehyde (38) carvomenthone (40), 1(7)-p-menthene-2-01 (42), and carvotanacetol (44).



37 38 42 40 44

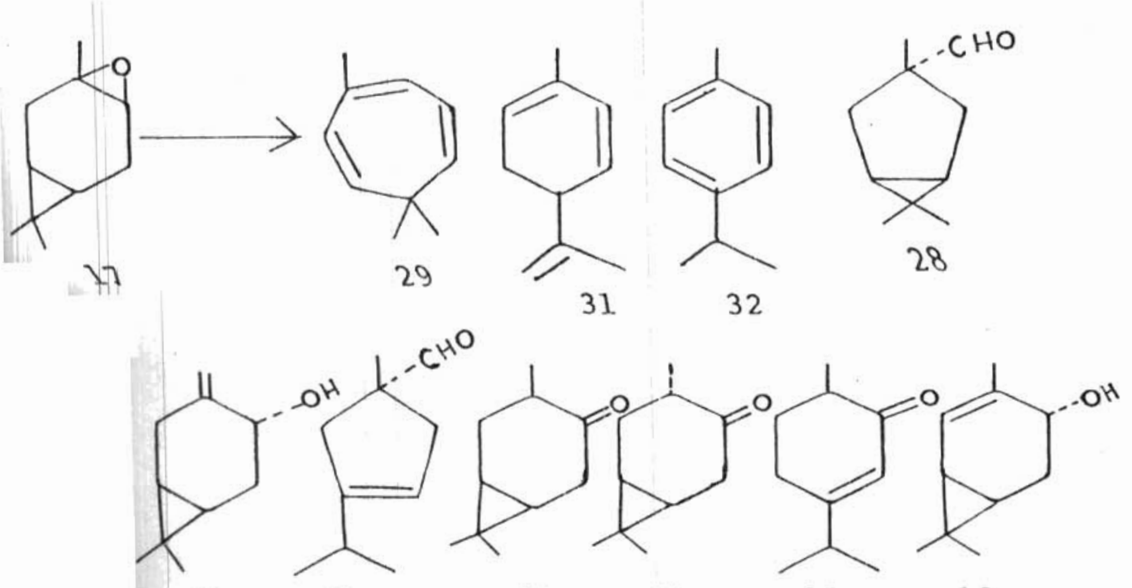
Over acidic catalysts like SiO_2-Al_2O_3, SiO_2-TiO_2 and zeolite *H-F9* a large amount of aldehyde (38) and ketone (40) were formed. *The selectivity for carbonyl compounds* were 90%. The formation of these compounds show the presence of a tertiary carbonium ion as the intermediate in the reaction course. Over catalysts like H_2SO_4/SiO_2, $FeSO_4$, $NiSO_4$ and $LiClO_4$ *the ketone (40)* was preferentially formed. The tertiary carbonium ion formed by the breaking of an α-bond of oxygen adsorbed on the strong acid sites of SiO_2-Al_2O_3 and SiO_2-TiO_2 are strong enough to attack the 3-position of the cyclohexane ring to form a five-membered ring, while carbonium ion formed by relatively weak sites of H_2SO_4/SiO_2,

$FeSO_4$, $NiSO_4$ or solid H_3PO_4 does not seem to be so. A hydrogen at the 2-position of the ring seems to migrate as a hydride ion to the cleaving tertiary centre during the course of the formation of a weak carbonium ion.

As in the case of d-limonene oxide, TiO_2-ZrO_2 showed remarkable activity for the formation of allyl alcohol and the alcohol with endo-double bond exceeded the one with exo double bond.

When Al_2O_3 was used as a catalyst for isomerization the product distribution largely varied with the type of alumina used in the reaction.

As a part of a series of studies dealing with the rearrangement of epoxides over heterogeneous acid and base catalysts, Arata and his co-workers carried out isomerization reactions of 2- and 3-carene oxides over heterogeneous catalysts[102,103]. The reaction products of 3-carene oxide were 3,7,7-trimethyl tropilidine (29) 1,5,8 (9)-p-menthatriene(31),p-cymene(32) 3,6,6-trimethyl bicyclo [3,1,0] hexane-3-carbaldehyde (28), 1-methyl-1-formyl-3- isopropyl cyclopent-3-ene (45), isocaranone (46), caranone (47), carvenone (35), trans-2-carene-4-01 (19) and trans-3(10)-carene-4-01 (18). The catalysts used were selected on its activity for isomerizations of d-limonene oxide and carvomenthene oxides.



17 29 31 32 28

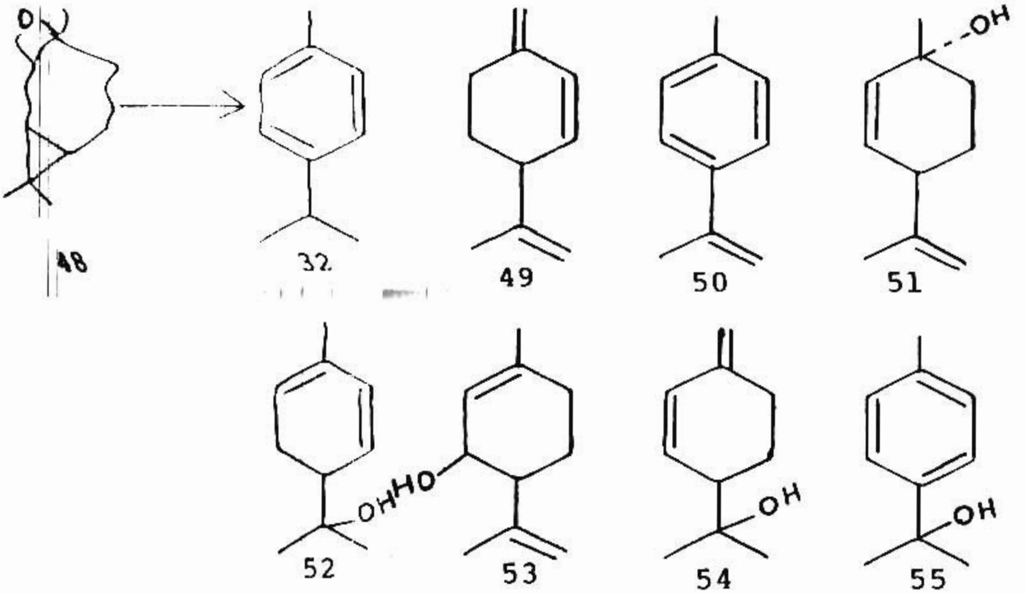
18 45 46 47 35 19

The main products with various catalysts were carbonyl compounds and allylic alcohols with a three membered ring except for the case of H_2SO_4/SiO_2 which produced large amount of p-cymene, cavenone and 1-methyl-1-formyl-3- isopropyl cyclo pent-3-ene were formed predominently over SiO_2-Al_2O_3 and $FeSO_4$, while allylic alcohols were formed preferentially over TiO_2-ZrO_2.

Most of the products with H_2SO_4/SiO_2 resulted from the opening of three-membered ring. In this case sulphuric acid supported on SiO_2 dissolves in the medium and clevage of the epoxide and cyclopropane ring results in free acid catalysis. Carvenone (35) may be formed from isocaranone and caranone. Among caranone and isocaranone, the most stable isocaranone (46) was formed predominently.

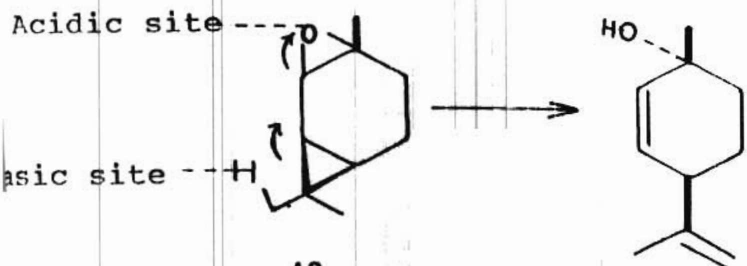
TiO_2 - ZrO_2 produced trans-2-caren-4-01, while TiO_2 produced trans-2-caren-4-01 and trans-3(10)-caren-4-01 in equal amounts. When Al_2O_3 was used as a catalyst in the isomerization, the product composition varied largely with preparation conditions of Al_2O_3. In all cases carbonyl compounds and allyl alcohols were present among the products.

In the isomerization of 2-carene oxide (48), the products were p-cymene (32),1(7),2,8(9)-p-menthatriene(49), α,-p-dimethyl-styrene (50), cis-2,8(9)-p-menthadiene-1-01 (51),α-phellandren-8-01(52),cis and trans-1,8,(9)-p-menthadien-3-01(53),β-phellandren-8-01(54) and p-cymen-8- 01(55).



The reactivity of 2-carene oxide was very high when compared to 3-carene oxide, but very few catalysts were inactive. All products obtained were resulted from the opening of the epoxide ring. Over catalysts like lithium diethyl amide in a heterogeneous system[104], 2-carene oxide yielded allylic alcohols with retention of cyclo propane ring. In the case of 2-carene oxide clevage of c(2)-0 is favourable than the c(3)-0 bond of 3-carene oxide. cis-2,8 (9) - p - menthadien-1-01 on acidic sites dehydrated to give cymene through a stable tertiary carbonium ion intermediate. $SiO_2-Al_2O_3$ produced a completely dehydrated product on its strong acidic sites, the reaction of HCl/SiO_2 was similar to $SiO_2 - Al_2O_3$.

The formation of cis-2,8(9)-p-menthadien-1-01 can be interpreted by accounting the greater stability of cyclopropyl carbinyl cation[105]. The clevage of the α-bond of oxygen, adsorbed on an acid site of the catalyst, is more favourable which is then followed by opening of the cyclopropane ring. TiO_2-ZrO_2 showed greater selectivity for the formation of cis-2,8(9)-p-mentha dien-1-01 which acts as a bifunctional catalyst with the abstraction of a proton from C-9 by a basic site facilitates opening of the 3-membered ring by the push effect of the anion.

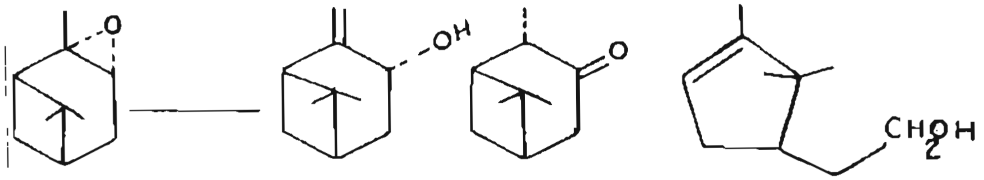


48

51

Compounds α-phellandren-8-01 (52), β-phellandren-8-01 and p-cymen-8-01 were formed by hydration of 2-carene oxide or cis-2,8(9)-p-menthadien-1-01 and subsequent dehydration on acid sites or dehydrogenation on basic sites. In presence of metatitanic acid 2-carene oxide gave 85% cis-iso limonenenol (51) in hexane at 70°C for 1 hr reaction[106].

2α,3α- Epoxypinane on treatment with Al_2O_3 is converted to trans-pinocarveol (10), pinocamphone (11) and α-campholenic alcohol (21)[87]. The selective formation of trans-pinocarveol (10) from the epoxide in a homogeneous catalytic system was carried out with basic media such as pot-t-butoxide in pyridine or N,N-dimethyl formamide[119], $LiAlH_4$ in cyclohexane[108] and $LiNEt_2$ in ether-benzene or $LiAlH_4$ in tertiary amine[109].



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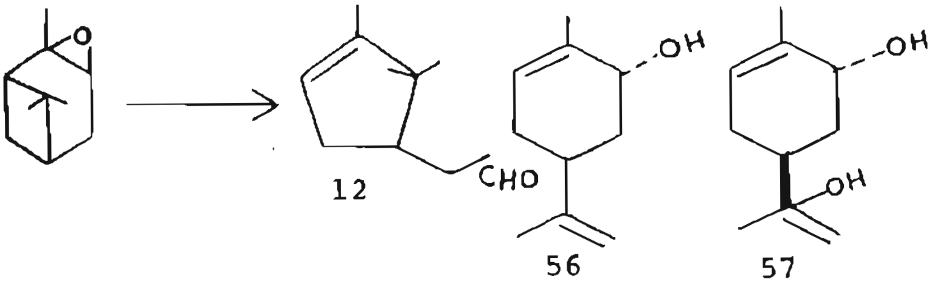
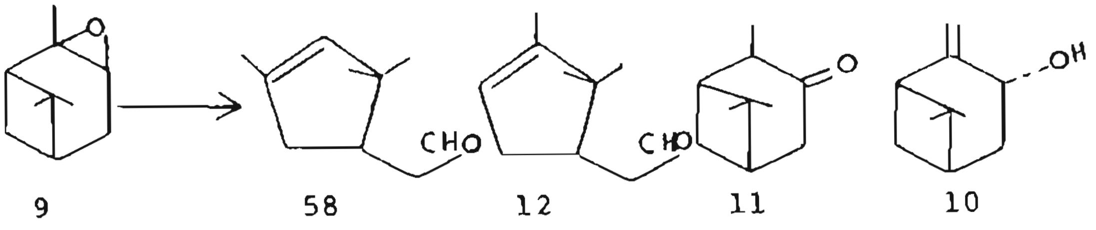
Joshi et al. obtained α-campholenic aldehyde (12) as the main product from the rearrangement of α-pinene oxide on silica gel. Minor products were trans-carveol (56) and trans-sobrerol (57)



The selective formation of α-campholenic aldehyde from the epoxide with acidic media is also observed in the homogeneous system with BF_3 etherate[110], $ZnBr_2$[110-112] and p-toluene sulphonic acid[113].

Arata and Tanabe investigated systematically the isomerization of α-pinene oxide over various acid-base catlysts[114] like SiO_2-Al_2O_3, H_3PO_4, Al_2O_3 and other metal oxides, metal sulphates etc. The main products were 1,2,4-trimethyl-3-cyclo penten-1-acetaldehyde (58), α-campholenic aldehyde (12), pinocamphone (11) and trans-pinocarveol (10).



The reactivity was very high in comparison with d-limonene, carvomenthene and 3-carene oxides, though the reactivities with TiO_2-ZrO_2 were not so high. The high reactivity seems to be due to the large strain energy of the 4-membered ring. The main products with various catalysts were aldehydes like 2,2,4-trimethyl-3-cyclo penten-1-acetaldehyde, α-campholenic aldehyde and allylic alcohol. The aldehydes were formed predominently over SiO_2-Al_2O_3, SiO_2-TiO_2, solid H_3PO_4, $FeSO_4$ and $NiSO_4$ with the selectivities more than 86% to aldehydes, whereas allylic alcohol was produced preferentially by TiO_2 and ZrO_2 with a selectivity of more than 80%. Large amounts of aldehyde and etone with low yield of allylic alcohol were formed over iO_2-ZrO_2 and aluminas, which showed high selectivity for ormation of allyl alcohol in reactions of d-limonene, arvomenthene and 3-carene oxides.

.9.2 Rearrangement of Terpenes

The first isomerization of 2-pinene in a liquid hase over solid catalysts was done by Gurvich in 1915[115]. ince then a number of studies have been reported and oducts were bi-and tri-cyclic terpenes such as 2(10)-nene,camphene,1,7,7,-trimethyl tricyclo [2,2,1,0] heptane, ornene, fenchene and monocyclic terpenes such as p- or enthadienes, p- or m-cymene and polymers.

Some of the products obtained from isomerization of terpenes are industrially important raw materials. Citronellol which is used in perfumery, is synthesized from 2(10) - pinene[116]. The reaction products of 2-pinene largely depended on solvents and type of acids. Monocyclic terpenes are produced in highly polar solvents like $H_2O-H_2SO_4$, CH_3 $COOH-H_2SO_4$, while medium polar solvents yielded bicyclo compounds like camphene, fenchene, bornene, 2(10)-pinene is formed in highly non-polar media such as small amount of HBr or benzoic acid in hydrocarbon solvents[117,118].

On the other hand, solid acid catalysts like mineral clay, silica-alumina, alumina, TiO_2, aluminium phosphate promote isomerization of 2-pinene. The acid sites on the surface of the catalysts play an important role in the izomerization reaction[119]. For this purpose, the catalytic activities for the isomerization of 2-pinene was compared with acid strength and a rough correlation between them was found[119-121]. The catalytic activity of a catalyst exceeds the activity of other catalyst that has a stronger acid strength but less acidity than the former. An acid catalyst, which has the highest acidity at an acid strength of $Ho \leqq -5.6$ and no acidity at acid strength stronger than $Ho \leqq -5.6$ will produce bi- and tri-cyclic monoterpenes of which main constituent is camphene.

Liquid bases like organoalkali metal in pentane-KOH or t-BuOK in DMSO promote interconversion between 2- and 2(10)-pinene similar to the case of acids in non-polar solvents[121-123]. Alkaline earth oxides catalysed isomerization reaction with high selectivities. In all these reactions high vacuum was maintained. Catalytic activity of CaO appeared when evacuated at 500°C and attained maximum at 600°C and decreased with higher evacuation temperature. Surface area of CaO at different temperatures were measured and its value decreased with calcination temperature. Higher activity observed at higher temperature was due to the appearance of more active sites at higher temperatures of calcination. In the case of SrO, maximum activity was observed at 1100°C calcined sample and the reaction reached equilibrium after 15 minutes of reaction. BaO showed maximum activity when catalyst was calcined at 1100-1300°C. When calcium, strontium and barium carbonate were used as precursors for catalyst preparation the compound should be calcined in vacuum at 600, 900 and 1100°C which are the dissociation temperature of corresponding carbonates. By calcination all CO_2 from the carbonates are removed to give very strong basic sites.

In the case of nickel sulphate maximum activity was observed when calcined at 400°C, indicating Lewis acid sites are active for isomerization reaction. If Lewis acid are active for isomerization, typical Lewis acids such as BF_3, $AlCl_3$ or $TiCl_4$ would catalyze the isomerization, but catalysts like BF_3, $AlCl_3$ or $TiCl_4$ yielded polymers only showing Lewis acids are converted to Bronsted acid site by adsorption of 2-pinene and the converted site is active for isomerization. The same mechanism was suggested for butene isomerization by Ozaki and co-workers[124]. In general the active sites for the isomerization of 2-pinene are considered to be Bronsted acid sites.

Many workers by kinetic studies revealed that the isomerization proceeded two separate and one way paths after forming a common intermediate between 2- and 2(10) - pinene. One of the paths give monocyclic terpenes and other gives rise to bi-and tri-cyclic terpenes. The presence of a common intermediate between 2- and 2(10) - pinene was evidenced by the fact that 2-pinene isomerized to form the products with same distribution as 2(10)-pinene[119,123]. The measurement of isomerization products during reaction gives an idea of path of the reaction. In presence of 2-piene, the isomerizations of camphene and 1,8-p-menthadiene are suppressed due to preferential adsorption of 2-pinene against camphene, menthadienes and others on the catalyst surface[124]. When camphene and 1,8-p-menthadiene were recemized over solid acids in the absence of pinenes the reaction produced, but in presence of pinenes, the reactions were suppressed. When optical yields of camphene and 1,8-p-menthadiene on nickel sulphate calcined at 250 and 450°C were plotted against the progress of isomerization, the long flat straight lines obtained showing a decrease in the optical yield with progress of reaction. These results support one-way paths for the course of the reaction. The optical yields of camphene and 1,8 p-menthadiene produced from 2-pinene took values identical with those of 2(10) - pinene, proves the preasence of a common intermediate between 2- and 2(10)- pinene. Every optical yield for camphene and 1,8-p-menthadiene took positive values, indicating that the configuration of an asymmetric centre of the reactant and the products are the same, while 1,8-p-menthadiene was produced by a different reaction pathway involving the attack of a proton of a cyclo butane ring. From the mechanism of inter conversion reaction between 2- and 2(10) - pinene over Pd/Al_2O_3 and raney Ni, an intermediate for the reaction should be of the alkyl type, since adsorbed hydrogen was essential to activate the catalysts. The intermediate over alkaline earth metal oxides were π -allyl anion type.

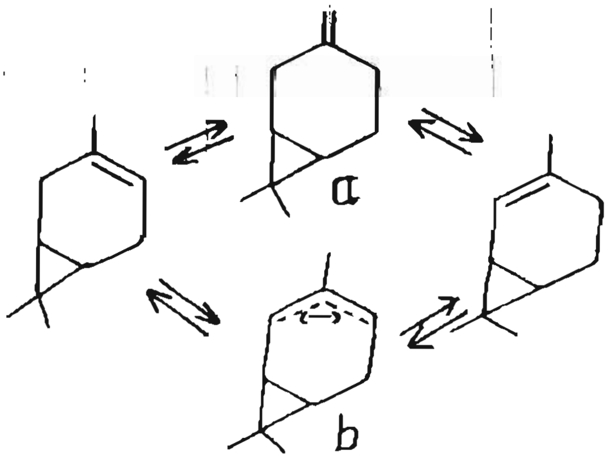
To determine the mechanism of interconversion over solid bases, a liquid base was taken as model catalyst[125]. No reaction was observed for 2-pinene over dimsyl sodium catalyst in DMSO-d_6 but isomerization of 2(10)-pinene with same catalyst system took place. 2-and 2(10)-pinene picked deuterium, with first deuterium incorporation of 2(10)-pinene at C_3-trans to gem-dimethyl group. In this system the bulkiness of the gem-dimethyl group prohibits reagents or solvent approaching cis-side of the group.

Booth found the activity of 3-carene as an industrial raw material for 1-menthol, which was used in perfumery, in pharmaceuticals and as flavouring in tooth paste, chewing gum and cigarettes. The first step in the reaction is the conversion of 3-carene to 2-carene over metal oxide catalysts. In 1975 Tanabe initiated the activity of finding suitable metal oxide catalysts for conversion of 3-carene to 2-carene[126]. The reaction was carried out in microcatalytic pulse reactor connected to a gas chromatograph. A one or 3 μl pulse of 3-carene was injected in to a helium stream and products were trapped at -196°C and then evaporated to column and analysed. The main products are 3- and 2-carene, 1,5-1,3-1,8 and 1,4-p-menthadienes, p-cymene, 1,4(8)- and 2,4(8)-p-menthadienes. 2-carene was largely formed over MgO, CaO prepared from $CaCO_3$, SrO, Y_2O_3 and ZrO_2. BaO, ZnO and ThO_2 poduced only p-cymene. On the other hand, Al_2O_3, Ce_2O_3, TiO_2 and SiO_2 - Al_2O_3 which are solid acids catalysed the reaction to form mainly various menthadienes and p-cymene[127].

Selective formation of 2-carene from 3-carene was reported over basic catalysts like Na or K metal on

Al_2O_3[128], organoalkali metal, pot tert-butoxide[128,129], lithium ethylene diamine[126,128]. Since MgO, CaO, SrO, Y_2O_3 and ZrO_2 are reported to be solid bases[132,133], the preferential formation of 2-carene may be due to the action of basic sites.

In the case of MgO and CaO they became active by pre-treatment at 500 and 700°C since these temperatures are the decomposition temperatures of their salts. At these calcination temperatures basic sites are produced on the surface of the catalyst. Over basic catalysts like MgO, CaO and ZnO a mechanism involving π -allylic anion intermediate was proposed for double bond migration in olefins[98,131]. By applying this mechanism to the isomerization of 3-carene to 2-carene two types of reaction paths are possible one passes through 2(10) - carene (a) and other through an anion (b).



Since catalysts have the ability to activate terium[134,135] exchange reaction, with deuterium is an efficient way to elucidate reaction path for isomerization. From the experimental data, allylic hydrogens in a ring (hydrogens on C-2 and C-5 in the case of 3-carene and hydrogens on C-4 of 2-carene) exchanged easily than the allylic hydrogens out of a ring and olefinic hydrogens were not substantially exchanged. Only one side of carenes can interact with the surface of the catalyst, because of the bulkiness of the gem-dimethyl group. The allylic hydrogens, which are towards the catalyst surface, will be abstracted and deuterated species are formed by picking up a deuterium atom from the surface. Thus deuterated species will have a deuterium which is always located on the side accessible to the surface.

1.10 Organisation of the Present Work

In the present work the author has conducted isomerization reactions of terpenyl oxiranes like (+) and (-)-limonene oxide, 3-carene oxide, α and β-pinene oxides and ar-curcumene oxide over chemically mixed catalysts like Al_2O_3-Y_2O_3, Al_2O_3-Sm_2O_3, Al_2O_3 - Eu_2O_3, Al_2O_3-Pr_6O_{11} and Al_2O_3 - Nd_2O_3. Most of the reactions reported on the isomerization of terpenyl oxiranes are described above and it is seen that there are no references of mixed oxide catalysts containing rare earth oxides.

Chapter II deals with preparation of different binary oxide catalysts in 1:1(w/w) ratio like Al_2O_3-Y_2O_3,

Al_2O_3-Sm_2O_3, Al_2O_3-Pr_6O_{11}, Al_2O_3 - Eu_2O_3 and Al_2O_3 - Nd_2O_3. The physico-chemical characteristics of catalysts were determined by chemical estimataion, surface area, pore volume, acidity and basicity studies. XRD, ESCA, TGA and MAS ^{27}AI NMR of the catalysts were also taken.

Chapter III describes the heterogeneous reactions carried out with terpenyl oxiranes like α,β-pinene oxides, (+), (-) limonene oxides, 3-carene oxide and ar-curcumene oxide. Reactions were done at differnt temperatures and products were identified by GLC and GC-MS analysis.

In Chapter IV , Al_2O_3-Y_2O_3 catalysts were prepared in different compsoitions and their activities with (+) - limonene oxide studied. In Chapter V different methods of preparation was employed for Al_2O_3-Y_2O_3(1:1) catalyst and their activity in the isomerization of (+)-limonene oxide are discussed. Chapter VI gives summary and suggestions for future work.

CHAPTER - II

BINARY OXIDE CATALYSTS OF ALUMINA-RARE EARTH OXIDES-PREPARATION AND CHARACTERISATION

2.1 Introduction

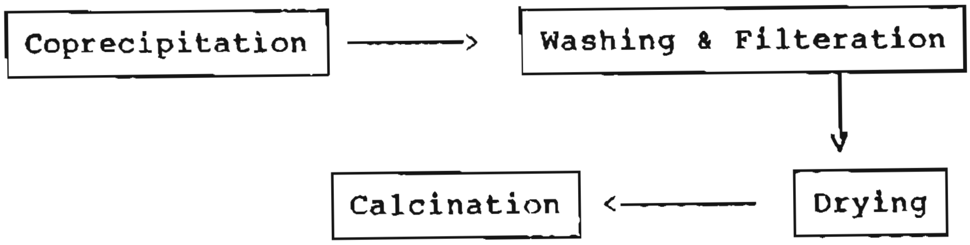
Method of preparation and characterisation of catalysts has become very important in catalytic reactions. The important factor looked for in a catalyst is its specificity giving high yields of the product. This specificity can be achieved only if the catalyst has high surface area, porosity, amorphous or crystalline nature coupled with acidic and or basic sites, stability and extended reaction life. The above attributes is highly dependent on the method of preparation of catalyst. The usual methods used for the preparation of catalysts are homogeneous and heterogeneous precipitations followed by washing with agents or solvents which will increase surface area, porosity and calcination at suitable temperatures. The latest use of sol-gel method is purported to give very high surface area.

A very important development in the area of catalysis which made a premier contribution in the field are zeolites. Zeolites are mainly aluminosilicates synthesized with the help of organic templates and heat treated.

In the present work, binary oxide catalysts of aluminium with rare earth metals like Yttrium, Samarium, Europium, Praseodymium, Neodymium were prepared and characterised. In this chapter, the methods of preparations of all these catalysts and characterisation has been described. A brief out line of the principle involved in different methods for characterisation of the catalyst is also attempted. The properties of the catalysts are correlated to preparation methods.

2.2 Preparation of Catalysts

Various steps involved in the catalyst preparation are schematically represented as below:



Scheme 1. Steps involved in the preparation of binary oxides

2.2.1. General Procedure for the Preparation of Catalysts

Principle

Alumina widely used as catalyst and support can be prepared with a wide range of surface areas and pore sizes[136,137]. The versatality in different phases is produced under different preparation and calcination conditions.

The most important method for the preparation of binary oxides is coprecipitation method of its mixed hydroxides. The raw materials for precipitation are selected in such a way that there should be least contamination of ions. Nitrates of common metals are preferred over sulphates and other salts, since they leave no contamination after calcination.

The factors which affect the catalyst texture in preparation are medium of precipitation, precipitating temperature, rate of stirring, presence of coprecipitating agent, pH and ageing time. The acidic and basic properties as well as the catalytic activities of mixed oxides vary with preparation conditions[98]. Lower temperature, higher stirring rates with short ageing time leads to high surface area catalyst. When coprecipitation is done for different oxides the precipitating rate of components may be different. In this instance, rate of stirring, pH of the solution, temperature of precipitation, ageing and precursor addition are important. For a homogeneous coprecipitation at constant pH, simultaneous addition of precursor solution is the best route. Usually in a coprecipitation method, NH_3 is used as the precipitating agent. The precipitates are formed in a non-uniform concentration of hydroxide ion. The mixed oxides prepared by this type of heterogeneous coprecipitation show higer acid strength. For producing easily filterable precipitate, precipitation from homogenous solution(PFHS) using urea as precipitant is used. Urea decomposes at elevated temperatures according to the equation

$$(NH_2)_2CO + H_2O \longrightarrow 2NH_3 + CO_2$$

$$NH_3 + H_2O \longrightarrow NH_4OH$$

NH_4OH formed precipitates the metals as its hydroxide. The precipitate formed will have a more uniform distribution of acid strength than that formed by heterogeneous method.

2.2.2 Washing and Filteration

Washing was performed by pouring 500 ml of wash solution over hydroxides on the filter and sucking dry. Filteration was done on vacuum filter with suitable filter paper. Number of washings depend on the presence of removable ions on the precipitate.

2.2.3 Drying

Drying is usually performed in an air oven at desired temperature. The primary purpose of it is to remove adsorbed water and sometimes water of hydration. Drying can also be done in an inert atmosphere or under vacuum in which gaseous atmosphere will not affect the catalyst. Heating rate and final temperature of oven are two variables which influence catalytic properties.

2.2.4 Calcination

This is a thermal treatment carried out for decomposing precursor compounds in the making of the catalyst. The catalyst will be porous and having mechanical strength after calcination. Nature and activity of catalyst materials differ greatly with the rate of heating and temperature of calcination. Usually calcination is carried out in a muffle furnace with a slow air flow to flush the furnace.

2.2.5 Experimental

Materials

The materials used are $Al(NO_3)_3 \cdot 9H_2O$ (E.Merck (India) Ltd; A.R.grade) Y_2O_3, Sm_2O_3, Pr_6O_{11}, Nd_2O_3, Eu_2O_3 (all 99.9% pure supplied by Indian Rare Earths Ltd; Alwaye). NH_4NO_3 (A.R grade supplied by E.Merck (India Ltd), NH_3 (25% solution, supplied by BDH) and 50% HNO_3 solution.

Method

In the present work, we used binary 1:1 oxides of Al_2O_3-Y_2O_3, Al_2O_3-Sm_2O_3, Al_2O_3-Pr_6O_{11}, Al_2O_3-Nd_2O_3 and Al_2O_3-Eu_2O_3. For comparative purpose along with binary oxides single oxides of Al_2O_3, Y_2O_3, Sm_2O_3, Pr_6O_{11}, Nd_2O_3 and Eu_2O_3 were also prepared. Single oxides were subjected to similar preparation and pretreatment conditions as that of binary oxides. Table 4 and 5 give the details of the catalysts prepared as well as the precursor solutions used for preparation.

Table 4

Quantities of Different Compounds used for the Preparation of Single Oxides

Oxide prepared	Quantity of precursor used in g			Amount obtained in g
	$Al(NO_3)_3.9H_2O$	NH_4NO_3	Rare earth oxide used	
Al_2O_3	370	-100	—	50.3
Y_2O_3	-	100	50.3	50.3
Sm_2O_3	-	100	50.3	50.3
Pr_6O_{11}	-	100	50.3	50.3
Eu_2O_3	-	100	50.3	50.3
Nd_2O_3	-	100	50.3	50.3

Table 5

Quantities of Different Compounds Used for the Preparation of Binary Oxide Catalysts

Oxide prepared	Quantities of starting components in g			Composition of catalyst
	$Al(NO_3)_3.9H_2O$	NH_4NO_3	Rare earth oxide	
Al_2O_3-Y_2O_3	370	100	50.3	1:1
Al_2O_3-Sm_2O_3	370	100	50.3	1:1
Al_2O_3-Pr_6O_{11}	370	100	50.3	1:1
Al_2O_3-Eu_2O_3	370	100	50.3	1:1
Al_2O_3-Nd_2O_3	370	100	50.3	1:1

2.2.6. Preparation of Single Oxide Catalysts

2.2.6.1. Preparations of Al_2O_3.

To an aqueous solution of $Al(NO_3)_3.9H_2O$ (370 g in 1000 ml distilled water), 150 g of NH_4NO_3 added. To the resulting solution 25% NH_3 added in excess with vigorous agitation. The final pH was 10. After ageing for 20 hrs, the precipitate was washed throughly with distilled water, filtered in vacuum, dried at 130°C for 24 hr and calcined at 400°C for 5 hr.

2.2.6.2. Preparation of Y_2O_3

50.3 g of Y_2O_3 was dissolved in minimum amount of 30% HNO_3 and the solution was diluted with distilled water to a volume of 900 ml. 100 g NH_4NO_3 was added to the solution. 25% NH_3 was added with vigorous agitation to a final pH 10. After ageing 20 hour the precipitated yttrium hydroxide was washed throughly with water. It was then filtered and dried at 130°C for 24 hr. The precipitate was calcined at 400°C for 5 hr. This procedure is followed for the preparation of other single oxides like Sm_2O_3, Pr_6O_{11}, [illegible]$_2O_3$, and Nd_2O_3. In all cases the oxides were calcined at 400°C for 5 hr.

2.2.7 Preparation of Binary Oxides

The hydroxides of binary oxides were prepared by coprecipitation. 370 g of $Al(NO_3)_3.9H_2O$ was dissolved in [illegible] water and solution was mixed with solution containing rare earth nitrate. Rare earth nitrate solution was prepared by dissolving required weight of rare earth oxide in minumum amount of 50% HNO_3. 200 g of NH_4NO_3 added to the mixed solution. 25% NH_3 solution was added with vigorous stirring. The precipitated hydroxides were aged for 20 hr in solution. The precipitate was washed with distilled water until it was free from nitrate ions. The precipitate was filtered under vacuum and heated to 130°C in an air oven for 24 hr and calcined at 400°C for 5 hr. The same procedure is followed for all binary oxide catalysts' preparation. Al_2O_3-Y_2O_3, Al_2O_3-Sm_2O_3, Al_2O_3-Nd_2O_3, Al_2O_3-Pr_6O_{11} and Al_2O_3-Eu_2O_3 used in this study were prepared in 1:1 (w/w) ratio.

Characterisation of Binary Oxide Catalysts

2.3 Chemical Analysis of Binary Oxide Catalysts

2.3.1 Principle

The rare earths were precipitated as their oxalates by oxalic acid from the binary oxide mixtures[138]. The oxalate was washed, filtered and ignited to oxide. From the weight of oxide obtained, the weight of alumina in the binary mixture was determined. Table 6 gives the chemical estimation values of different binary oxides used.

2.3.2 Procedure

1 g of the catalyst was accurately weighed and dissolved in dilute HCl by boiling. The solution was diluted to 250 ml, neutralized most of the acid by adding NH_3 solution, followed by a drop of methyl violet indictor. The color of the solution was adjusted to blue-green by addition of HCl or NH_3 solution. The solution was heated to boiling and a saturated solution of oxalic acid (12%) was added with constant stirring. A crystalline precipitate started forming after one minute. The solution was boiled for 3 minutes again and cooled overnight with occasional stirring. The precipitate was filtered on a whatman No.40 filter paper. The precipitate was washed repeatedly with 2% w/v oxalic acid and 1% v/v concentrated hydrochloric acid. The filter paper was transferred to a previously weighed silica crucible and ignited from $900^{o}C$ to $1000^{o}C$ for 1 hr. The crucible was cooled in a desiccator, weighed. Heating, cooling and weighing continued till constant weight is obtained. From the weight of rare earth oxide, weight of alumina in the binary oxide mixture was determined.

Table 6

Chemical Estimation Values of Different Catalysts

Catalyst 1:1	Chemical estimation value w/w
Al_2O_3-Y_2O_3	1:0.952
Al_2O_3-Sm_2O_3	1:0.920
Al_2O_3-Pr_6O_{11}	1:0.931
Al_2O_3-Eu_2O_3	1:0.952
Al_2O_3-Nd_2O_3	1:0.943

2.4. Surface Area

2.4.1. BET Technique

Measurement of surface area of solid materials is classically performed by method developed by Brunauer, Emmett and Teller (BET Method)[139].

2.4.2. Principle

In this method, pre adsorbed gases and vapours from the solid surface is removed. Then solid is cooled to the boiling point of adsorbate gas. The solid surface is incremently exposed to higher partial pressures of adsorbate gas until the entire surface is covered by one molecular layer of the gas. The extent of the surface of the solid can be calculated by multiplying the number of molecules of adsorbate gas required to form the monolayer times the area covered by each gas molecule.

Temperature is held constant in this method and amount of nitrogen adsorbed at liquid nitrogen temperature (-196°C) is measured at several pressures.

If n_m is the volume of nitrogen adsorbed in a monolayer then BET equation can be written as

$$\frac{P}{n(P^o - P)} = \frac{1}{n_m c} + \frac{c - 1}{n_m c} \frac{P}{P_o} \longrightarrow (8)$$

where P^o - vapour pressure of nitrogen at adsorption experiment.

P - nitrogen pressure.

n - volume of nitrogen adsorbed at pressure P and the temperature of liquid nitrogen calculated to STP.

C - constant related to the difference between the heats of liquefaction and adsorption of the adsorbate.

A plot of $P/n(P^o - P)$ versus P/P^o will be lenear a range of pressures from 0.05 to 0.35 where S is the e equal to $c-1/n_m c$ and intercept 'i' equals $1/n_m c$

$$S + i = \frac{1}{n_m c} + \frac{c-1}{n_m c} = \frac{1}{n_m} \longrightarrow \quad (9)$$

$$\therefore \; n_m = \frac{1}{s+i} \longrightarrow \quad (10)$$

n_m can be determined by adsorption, surface area 's' can be obtained from the equation

$$S = \frac{NAn_m}{V_m w}$$

Where N = Avagadro's number 6.024 x 10^{23} molecules/g

A = area occupied by one nitrogen molecule in the liquid nitrogen state, 16.3x10^{-20} m^2.

n_m = g. molar volume 22400 ml

w = sample weight in g.

2.4.3. Procedure

Adsorption and desorption occur when the sample is immersed in to and then withdrawn from a liquid N_2 bulb. Changes in the ratio of nitrogen to helium in the flowing s stream due to adsorption and desorption are sensed as arly gausian shaped signals by a specially designed ermal conductivity detector. The instantaneous signal ight is proportional to the rate of adsorption or orption and the total integral area under the curve is portional to the quantity of gas adsorbed. This area is omatically integrated by the equipment (Quantasorb Jr.).

calibration of this integrated desorption signal with a known volume of adsorbate produces an accurate measure of the adsorbed volume. Table 7 gives the surface area values of different catalysts obtained by BET method.

Table 7

Specific Surface Areas Obtained for Various Catalysts by BET Method

Catalyst	Surface area m^2/g
Al_2O_3-Y_2O_3	101.8
Al_2O_3-Sm_2O_3	97.35
Al_2O_3-Pr_6O_{11}	42.517
Al_2O_3-Eu_2O_3	101.25
Al_2O_3-Nd_2O_3	121.507

2.5 Pore Size Distribution:

Most common method to find the pore size is mercury intrusion technique.

2.5.1 Apparatus

The equipment used in the present study is an Autoscan 60 porosimeter.

2.5.2 Principle

The technique of mercury porosimetry consists essentially in measuring the extent of mercury penetration into an evacuated solid as a function of applied pressure. Mercury unlike other liquids, has a positive angle of contact with most of solid catalyst materials hence pressure must be exerted for mercury intrusion in to the pores.

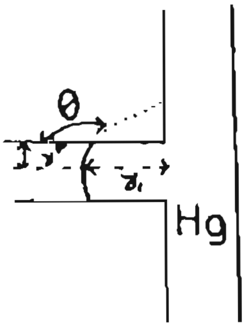


Fig.3 **Mercury penetrating a cylindrical pore**

The technique of mercury porosimetry was orginally developed to enable pore sizes to be determined in the macropore range where gas adsorption method breaks down for practical reasons. Since the angle of contact of mercury with solids is nearly 140^o and therefore more than 90^o, an excess pressure γ^P is required to force liquid mercury in to the pores of a solid. The idea of using mercury intrusion to measure pore size appears to have been first suggested by Washburn who put forward the basic equation[140].

$$\gamma^{P} = \frac{2\cos\theta}{p} \longrightarrow \qquad (11)$$

Where γ^{P} is the radius of the pore, assumed to be cylindrical.

Equation (11) is the special case of the Young-Laplace equation.

$$p^{Hg} - p^{g} = -\gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \longrightarrow \quad (12)$$

where p^{Hg} is the course of pressure on mercury phase and p^{g} that in the gaseous phase. Since the meniscus is a segment of a sphere

$$r_1 = r_2 = \gamma^{P}\cos\theta$$

and $\quad p^{Hg} - p^{g} = \Delta p$

is the pressure which must be exerted on the mercury to force it into a cylindrical pore of radius γ^{P}. These insertions in equation (12) with slight rearrangment, lead directly to the washburn equation (11).

The method consists in measuring the extent of mercury penetration into an evacuated solid as a function of the applied hydrostatic pressure. In 1945 Ritter and Drake developed this technique for high pressures. The range of the porosimeter extended from $\gamma^{P} \sim 35$Å to $\gamma^{P} \sim 7.5$ µm, the size of pore penetrated at atmospheric pressure. In some experimental designs the pore size range is extended to

15Å by increasing the maximum applied pressure to ~ 5000 bar and at the upper end by reducing the applied pressure below atmospheric pressure. Gas adsorption method has considerably overlapped by mercury intrusion method. Gas adsorption at the upper end of the mesopore range and mercury porosimetry at the lower end are applicable. Contact angle of mercury, like that of other liquids, depends not only on whether mercury is advancing over, or receding from the solid surface, but also on the physical and chemical state of surface itself.

In mercury porosimetry the volume v of mercury taken up by the solid is measured as the applied pressure $(p^{Hg}-p^{g})$ is increased. The value γ (Hg) at any value of applied pressure Pi therefore gives the volume of all pores having a *radius* equal to or greater than γi^{p} and is called cumulative pore volume. In this technique cumulative pore volume v decreases as γ^{p} increases, where as in gas adsorption $\Sigma(\partial v i^{p})$ increase with increasing γ^{p}.

By measuring changes in volumetric penetration as the pressure p in dynes per square centimeter is changed, the volume of pores in various size ranges as calculated from the washburn equation can be determined.

2.5.3 Procedure

A known weight of the sample was taken in the cell of porosimeter. The cell was filled with mercury and evacuated by applying high vacuum. Without breaking vacuum excess of mercury was drained off. The cell was then transferred to the metallic cup of the porosimeter and the position of the cell was adjusted and pressure increased gradually to 60 kPsi. After reaching the maximum value, pressure was allowed to fall off. From the intrusion data the pore size distribution and total pore surface area was obtained with the help of a computer. Table 8 gives the total pore surface area of different catalysts. The pore size distribution of various catalysts obtained by mercury intrusion method is given in Fig 4.

Table 8

Total Pore Surface Area Values of Different Catalysts Obtained by Mercury Intrusion Method

Catalyst	Sample wt g	Total pore surface area m^2/g
Al_2O_3-Y_2O_3(1:1)	0.4560	30.64
Al_2O_3-Sm_2O_3(1:1)	0.3990	37.87
Al_2O_3-Nd_2O_3(1:1)	0.3980	21.79
Al_2O_3-Eu_2O_3(1:1)	0.4200	28.39
Al_2O_3-Pr_6O_{11}(1:1)	0.4050	4.43

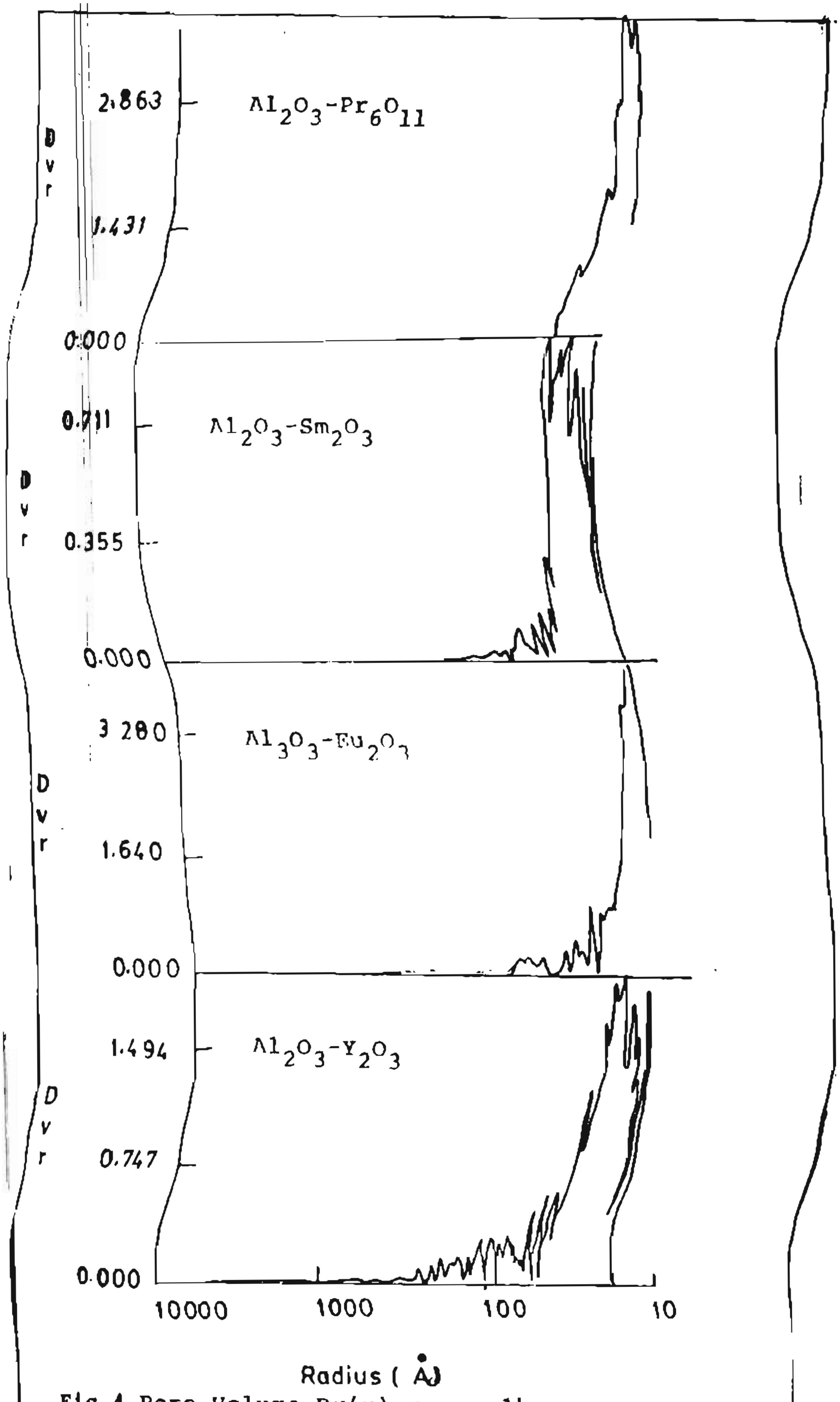


Fig.4 Pore Volume Dv(r) vs radius

2.6 X-ray Diffraction Method

This method is the most widely used technique for identification and characterisation of materials, since it is non-destructive.

2.6.1 Principle

X-ray diffraction can be visualized as a reflection of the incident beam by parallel closely spaced planes of atoms within a crystal. The condition for reflection is the well known Bragg equation

$$n\lambda = 2d\sin\theta$$

X-rays are electromagnetic waves and of shorter wave length. They are generated when high velocity electrons impinge on a target. From Bohr structure of atom, the critical voltage to generate these rays is that which gives the bombarding particle sufficient energy to eject one of the shell electrons from the target atom. when this happens an electron from one of the outer shells immediately negotiates a jump replacing the dislodged electron and emitting a quantum of radiation. A monochrmatic beam of x-rays were produced from the selective filter in the instrument. Interference of electromagnetic waves over solid produce a diffraction pattern which is characteristic of its crystalline nature. No sharp diffraction pattern was observed for amorphous sample. A diffractometer consists essentially an x-ray generator, a goniometer for rotating the sample and measuring diffraction angles, and an X-ray counter tube and counting circuits to detect, amplify and measure the diffracted radiation. The diffractogram represent a permanent record of intensity against diffraction angle, and is obtained directly by a strip-chart recorder or by some out put device.

2.6.2 Procedure

Equipment used in the present study was pw 1710 Phillips Holland comprised of an x-ray tube working in the voltage range 35kv and electron emission current 10 mA. The eletron beam produced by the heated filament was focussed to the slender target area. Cukα radiation was used in the diffraction studies since it has long wave length and hence greater 2θ interval, and also copper has outstanding thermal conductivity. About 10 mg of the sample was spread on the sample holder. Sample was scanned at an angle 20-60^{o}. The XRD pattern of all single and binary oxides are given in Figs. 5 and 5'.

2.7 Thermogravimetric Analysis

The method of thermogravimetry is basically quantitative in nature that the mass change can be accurately determined. The temperature ranges in which the mass changes occur are qualitative and in that respect they depend on the instrumental and sample characteristics.

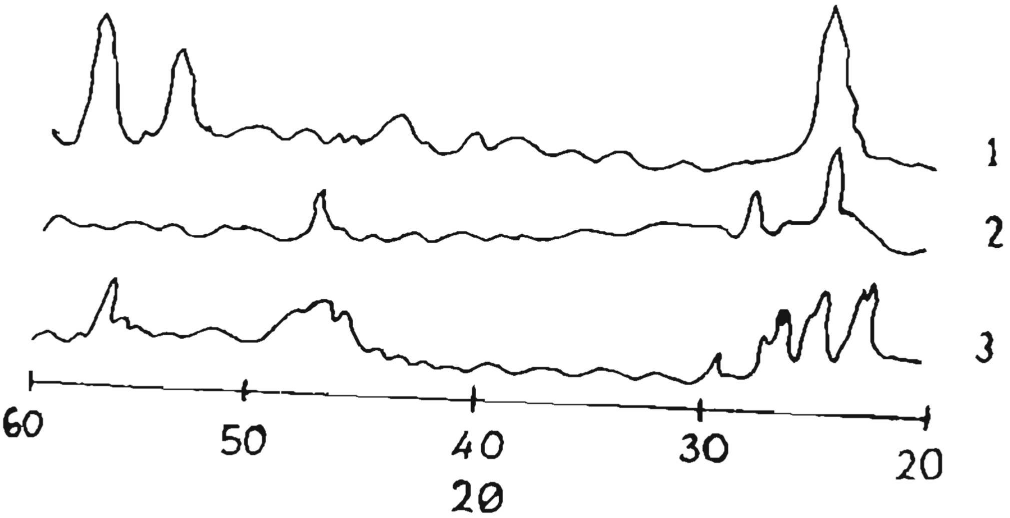


Fig. 5 -XRD spectra of different catalysts

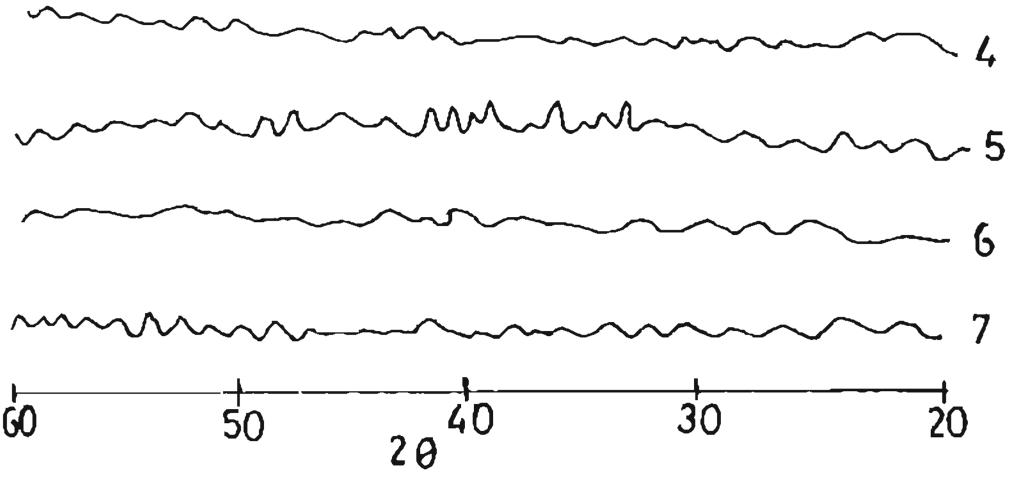


Fig. 5' XRD spectra of binary oxides

1. Y_2O_3 2. Eu_2O_3 3. Al_2O_3 4.Al_2O_3-Sm_2O_3(1:1)
5. Al_2O_3-Pr_6O_{11}(1:1) 6. Al_2O_3-Nd_2O_3(1:1)
7. Al_2O_3-Eu_2O_3(1:1)

2.7.1 Derivative Thermogravimetry.

Principle

In thermogravimetry, mass of a sample m is continously recorded as a function of temperature T or time t.

$$m = f(T \text{ or } t)$$

Quantitative measurements of the mass changes are possible by determination of the distance, on the curve axis, between the two points of interest or between the two horizontal mass levels.

In derivative thermogravimetry, the derivative of *mass change with respect to time* dm/dt is recorded as a function of time(t) or temperature (T) or

$$\frac{dm}{dt} = f\ (T \text{ or } t)$$

In other cases, the derivative of mass change with respect to temperature, dm/dt is recorded as a function of time (t) or temperature (T) as

$$\frac{dm}{dT} = f\ (T \text{ or } t)$$

In either case, the resulting curve is the first derivative of the mass change curve. A series of peaks are obtained in which the areas under the peaks are proportional to the total mass change of the sample. *DTG curve presents the* same information given by the TG curve in a visually accessible way, since the area under the DTG curve is proportional to mass change. The DTG curve allows the ready determination of the temperature at which the rate of mass change is maximum, and it provides additional information to the extrapolated onset temperatures. Dynamic thermogravimetry has been widely used to study the kinetics of thermal decomposition reactions.

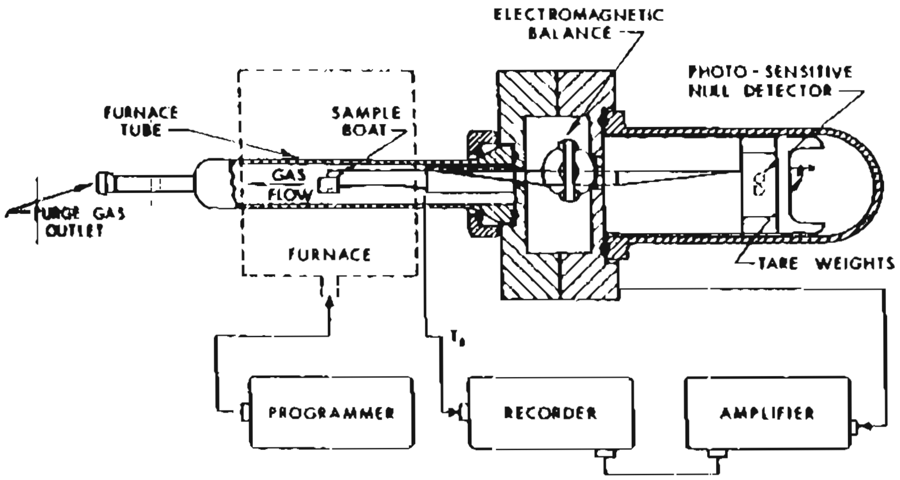


Fig.6 Dupont thermal balance

Thermobalance is an instrument that permits continuous weighing of a sample as a function of temperature. Modern thermo balance consists generally a recording balance furnace, furnace temperature programmer or controller and a recorder. The balance consists of a null-balancing, Stark apparatus to remove water. The benzene was refluxed over sodium, distilled and kept over sodium wire[145].

n-$BuNH_2$ (S.D Fine chemicals) was purified by distillation. About 0.1 M solution is prepared by weighing 1ml of n-$BuNH_2$ in 100 ml volumetric flask and making upto volume using purified dry benzene.

Indicators

Neutral red was obtained as the hydrochloride salt. *It was converted to the neutral base by adding slight excess of standardized sodium hydroxide solution. The product was washed several times and stored in a desiccator over* drierite. All other indicators enlisted in Table 9 were purified by recrystallisation. Indicator solutions were prepared by dissolving 0.1g of material in dry benzene.

2.8.2 Acid Strength Measurements

To determine the acid strength of catalysts, a variety of Hammett indicators are used. The Hammett indicators used in the present study are listed in Table 9 with their color changes and corresponding pKa' values.

Table 9

Indicators used for Acid Strength Measurements

Indicators	Basic color	Acid color	pKa
Neutral red	Yellow	red	+6.8
α-Naphthyl red	brown yellow	red	+4.0
Methyl yellow	orange	red	+3.3
4-phenyl azodiphenyl amine	brown yellow	purple	+1.5
Dicinnamal acetone	orange	brick red	-3.0
Benzal aceto phenone	colorless	yellow	-5.6
Anthraquinone	colorless	light yellow	-8.1

Experimental

1. Ten to fifteen grams of catalyst samples were calcined at 400°C for 5 hour. After the calcination period sample was allowed to cool while dry air is passed through the furnace. When the sample reached 150°C, it is transferred to screw cap bottles and stored in a desiccator.
2. Roughly 0.1 g of sample was transferred to a test tube, 5ml of dry benzene added followed by 5 drops of 0.1% indicator solution. Color developed on the catalyst

sample was noted. From the color change acidic or basic nature of the catalyst to various indicators in different pKa values were found.

2.8.3 Acidity of Catalyst Surfaces

Acidity of catalyst surface estimated by titration of n-$BuNH_2$ using various Hammett indicators by Benesi's[37] successive approximation method.

Experimental

1. Roughly 1 g of the calcined catalyst sample was transferred to weighed screw cap bottle kept in a desiccator. Screw cap bottle reweighed to obtain the sample weight correctly.
2. Ten ml of dry benzene was added to weighed samples. 0.1M n-$BuNH_2$ in benzene was added in successively increasing amounts. Screw cap tubes were capped and equilibrated in a shaker overnight at room temperture.
3. After equilibration, two ml portions of the catalyst suspensions were added to test tubes and tested with Hammett indicators. Test tubes were arranged in the order of increasing butylamine content and checked at which stage enough n-butyl amine was added to neutralize catalyst acidity to a particular indicator.
4. Steps 2 and 3 were repeated with smaller stepwise increase in the n-butyl amine content, so that

uncertainty in measuring the titer values will be very small.

The acid strength of all single and binary oxides were determined and are depicted in Tables 10 and 11 respectively. Steps 1,2,3,4 of the above procedure was repeatedly done to get the acidity of all binary oxides. The acidity in mmol/m^2 of various catalysts are given in Table 12.

Table 10

Acid Strength of Various Single Oxides

Catalyst	Ho range
Al_2O_3	-3.0 to -5.6
Y_2O_3	+3.3 to + 1.5
Sm_2O_3	+1.5 to -3.0
Eu_2O_3	+1.5 to -3.0

Table 11

Acid Strength of Various Binary Oxide Catalysts

Catalyst	Ho range
Al_2O_3-Y_2O_3	-5.6 to -8.2
Al_2O_3-Sm_2O_3	-5.6 to -8.2
Al_2O_3-Nd_2O_3	-5.6 to -8.2
Al_2O_3 - Eu_2O_3	-5.6 to -8.2

Table 12

Acidity Distribution of Binary Oxide catalysts

Catalyst	Acid amount in m mol/m^2 at various acid strength (Ho values)				
	+6.8	+4.0	+3.3	+1.5	-3
Al_2O_3-Y_2O_3	0.0589	0.0044	0.0021	0.0030	0.0001
Al_2O_3-Nd_2O_3	0.1074	0.5099	0.0123	0.0070	0.0028
Al_2O_3-Sm_2O_3	0.0924	0.4375	0.0292	0.0041	0.0071
Al_2O_3-Eu_2O_3	0.1135	0.4990	0.0350	0.0380	0.0088

2.8.4 Basicity

Materials

Cyclohexane, (E. Merck (India) Ltd, G.R. grade) benzene (G.R grade, E. Merck (India) Ltd) and benzoic acid (99.5% pure guaranteed reagent, supplied by BDH) are used in these studies. Indicators and their color changes at corresponding pKa values are given in Table 13.

Table 13

Indicators used for Basic Strength Measurements

Indicator	pKBH	Basic color	Neutral color
2,4,6-Trinitro aniline	12.2	Reddish orange	Yellow
2,4-Dinitroaniline	15.0	Purple	Yellow
4-Nitroaniline	18.4	Yellowish orange	Yellow
4-Chloroaniline	26.5	Pink	Colorless

2.8.5 Purification of Materials

Purification of cyclohexane

Cyclohexane was passed through a column of activated silica, and lithium aluminiam hydride added and distilled and kept over sodium wire. It was again distilled and kept on 4Å moleculer sieves.

Benzene was purified as in section 2.8.1. Benzoic acid was purified by recrystallisation and solution was made in dry cyclohexane. Indicators were dissolved in benzene to get 0.1 wt% solution.

2.8.6 Experimental

The method consists of titrating catalyst suspensions with benzoic acid using various nitroaniline indicators.

1. About 15 g of catalyst sample was transferred to glass sample tubes and calcined at 400°C for 5 hr. It was then cooled to 150°C and kept in a desiccator.
2. About 15g of catalyst sample was transferred to weighed screw cap vials. The sample weight was determined and 10ml of cyclohexane was added to each of them. Maximum care was taken to avoid contact of the sample with air while transferring.

3. Benzoic acid solution was added in successively increasing amounts to each of the samples. Samples were equilibrated for 5 hours in a shaker.

4. After equilibration 2ml each of catalyst suspensions were taken in test tubes and indicators added. Test tubes were arranged in increasing amount of benzoic acid content.

5. The color developed in each test tubes were noted after 24 hr. Titrations were repeated with small increments in the amount of benzoic acid, to reduce the amount of error. The end point, where basic color just disappeared was determined. The basic strength and basic amount of all binary oxide catalysts are given in Tables 14 and 15.

Table 14

Basic Strength of Various Binary Oxide Catalysts

Catalyst	H_- range
Al_2O_3-Y_2O_3	15 to 18.4
Al_2O_3-Sm_2O_3	15 to 18.4
Al_2O_3-Nd_2O_3	15 to 18.4
Al_2O_3-Eu_2O_3	15 to 18.4

the same energy. For most commercial ESCA instruments $h\gamma$, is either 1256.3 eV generated from a Mgkα anode or 1486.7 from an Alkα source.

In this device a heated tube provides electrons which are accelerated to a potential of between 10 and 20 kev towards a water cooled anode side. The electrons creat core holes in the anode atoms, which are filled by relaxing electrons from high levels. The relaxation process is followed by X-ray fluorescence. Several factors prefer Mg or Aluminium as anodes. The factors are a narrow line width of X-ray transition which is essential to obtain a narrow spread in observed E_B. The energy of the characteristic X-ray should be sufficient to excite photoelectron and Al has an advanced merit of higher melting point. The resulting X-ray from Aluminium will have large intensity hence good resolution.

2.9.2 Procedure

Photo electron spectroscopic measurements were carried out on an ESCA-3 Mk11 electron spectrometer (V.G Scientific U.K). Photo electrons were excited using Alkα radiation which were monochromatized by reflection from a quartz crystal. Sample was mounted on a sample holder and was cleaned by Ar^+ ion sputtering. In this method a beam of 500-5000eV Ar^+ ions with a current of 1-10 $\mu A/cm^2$ was focussed to the sample. These ions posseses considerable

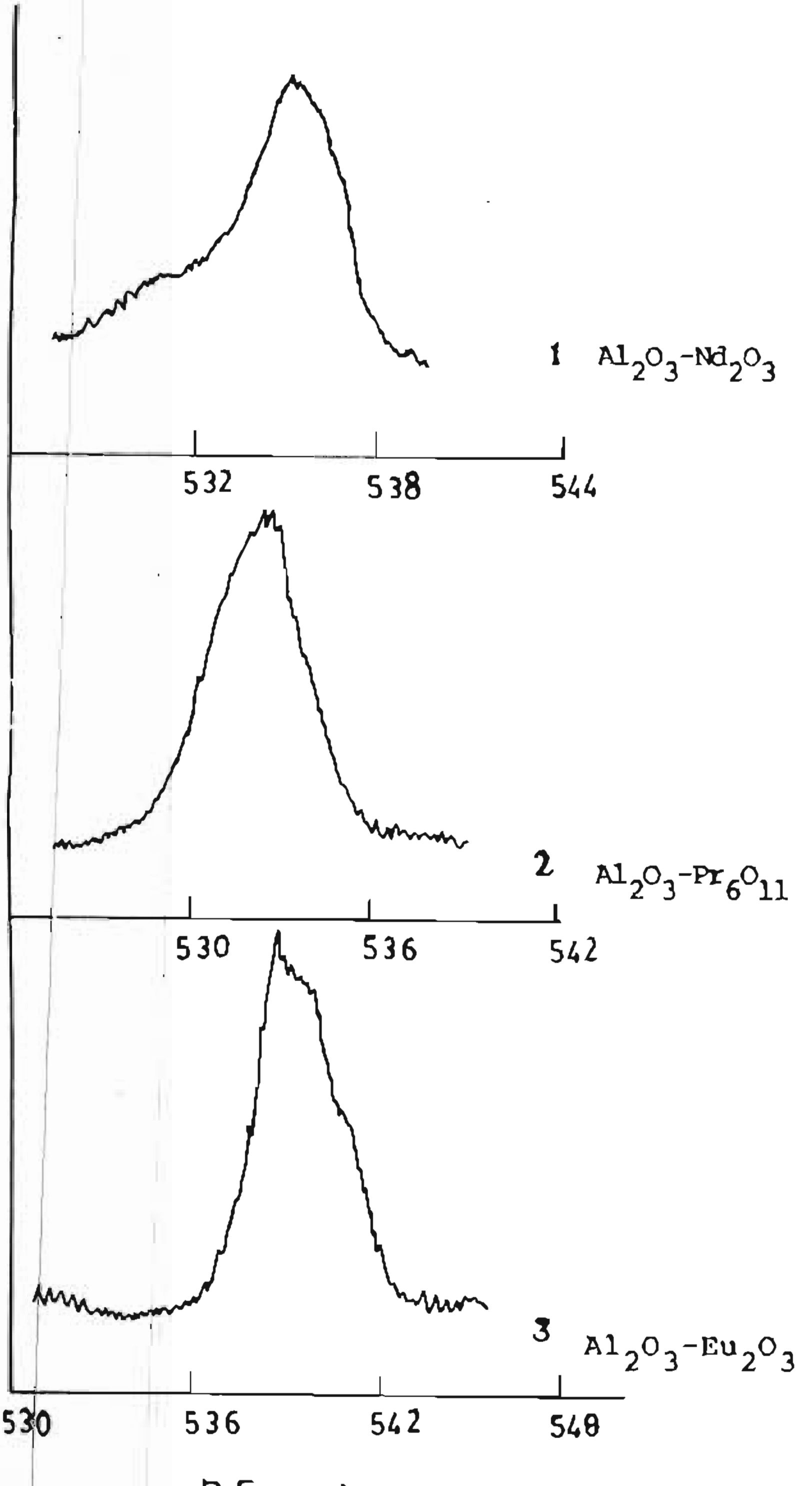


Fig. 10 XPS diagram of various catalysts

frequency there will be energy transition taking place between the spinning nucleus and radio frequency beam. This transition is called resonance and hence the term nuclear magnetic resonance. The precessional frequency 'γ' is directly proprotional to the external field Bo.

$$\gamma \propto Bo$$

Very broad NMR adsorption lines are obtained from solid samples because chemical shift amisotropy as well as dipolar and quadrupolar interactions which in solutions and liquids are averaged by the rapid thermal motion of the molecule are not so averaged in solids.

2.10.2 Procedure

^{27}Al has magnetic moment $I = 5/2$ and a chemical shift at the range of 450 ppm. So the peaks will be very broad. Magic Angle Spinning device was hence used. Instrument used was Brucker MSL 300 at 78.2 MHz. Sweep width was 250kHz with a pulse length of 1 μsec.

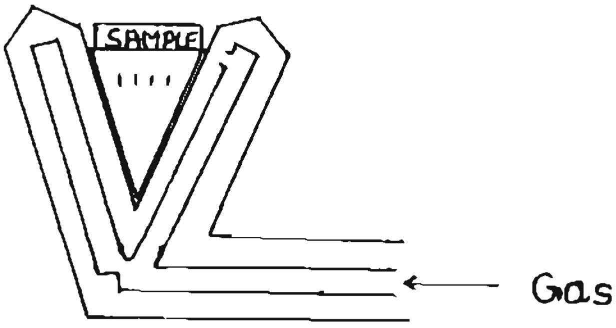


Fig.7 Sample keeping device in MAS ^{27}Al NMR

Compressed N_2 enters the space between the stator and the rotor through jet holes maintained at an angle to the conical mushroom surface of the rotor. The whole assembly was placed at 54°44' to the direction of applied magnetic field. Relaxation delay of the instrument was 500 ms. NaY-zeolite was used as the reference at 62.8 ppm. Sample was spun at the magic angle at the rate of 4.3 KHz and also at 3.34 KHz.

2.11 Results and Discussion

2.11.1 Catalyst composition

Binary oxide catalysts were prepared by precipitation as hydroxides from nitrate solution, the addition of ammonia solution in one lot with efficient stirring preclude the initial precipitation of rare earth hydroxides. The precipitate was throughly washed to free itself of nitrate ions and calcined at 400°C for 5 hr. The single oxide catalysts were also prepared in the same manner.

Gravimetric estimation of catalysts doesn't show much variation in the composition from theoretical values. This shows that during coprecipitation neither aluminium prevent complete precipitation of rare earth nor rare earths prevent complete precipitation of aluminium.

2.11.2 Surface Properties

2.11.2.1 Surface Area

The accessibility of a catalyst surface to reacting gases is of considerable importance in the selection of a solid material which is to function as an active catalyst for heterogeneous reaction. For a given catalyst, greater the amount of surface available to the reactant the better the conversion to products. Few catalyst meprations which are energetically homogeneous in the sense that all adsorption sites are equivalent and the same amount of energy is exchanged between each molecule of adsorbate and adsorbent site. If such a catalyst could be prepared, then its activity would be directly proportional to the surface area exposed to the reactant. Surface area measurement is an important expedient in predicting catalyst performance and determining the role which the catalyst surface plays in any heterogeneous reaction.

Table 7 gives the specific surface area results of alumina-rare earth oxide mixtures consisting of Pr_6O_{11}, Nd_2O_3, Sm_2O_3 Y_2O_3 and Eu_2O_3 (all 1:1 binary oxides). The surface area values determined by BET method ranged from 97.35 m^2/g to 121.507 m^2/g. The highest specific surface area values has been obtained for Al_2O_3-Nd_2O_3 system while Al_2O_3-Eu_2O_3 has got a value, 101.25 m^2/g. Even though the method of precipitation of catalysts were same, surface area of Al_2O_3-Pr_6O_{11} was found to be unusually low having a value of 41.51 m^2/g. This may be due to agglomeration during the formation of the mixed binary oxide. It is interesting to note that except Nd_2O_3 system the surface area are in tune with decomposition pattern presented in the thermogravimetric data. It appears that the increased surface area of Al_2O_3-Nd_2O_3 system is probably due to slow decomposition of the hydroxide mixture as it requires still higher temperature for complete decomposition on the other hand, from the reactivity data it appears that Al_2O_3-Eu_2O_3 system is more effective than the other binary oxide systems studied. Although Al_2O_3-Eu_2O_3 has got slightly lower surface area but possibly has sufficient microporosities which is quite possible because of the fast removal of hydroxyls from the system. This is true if we compare Al_2O_3-Eu_2O_3 system and Al_2O_3-Y_2O_3 system having near specific surface areas but different TGA patterns.

2.11.2.2 Pore Size Distribution

Pore volume Dv(r) distribution versus radius of various binary oxide catalysts are deplicted in Fig. 4. All five binary oxides show different patterns in pore size distribution. Pore surface area values calculated from mercury porosimetry are given in Table 8. Al_2O_3-Y_2O_3 showed a wide distribution of pore from 20Å to 1000Å and total pore surface area 30.64 m^2/g. For Al_2O_3-Sm_2O_3 pore size distribution ranged from 20-200Å. Al_2O_3-Pr_6O_{11} had a very narrow distribution of 20-25Å. Other catalysts Al_2O_3-Eu_2O_3 and Al_2O_3-Nd_2O_3 had a distribution of pore size between 20 and 70Å. Al_2O_3-Sm_2O_3 had a total pore area of 37.87 m^2/g while Al_2O_3-Pr_6O_{11} had a very small value of 4.43 m^2/g. Al_2O_3-Eu_2O_3 and Al_2O_3-Nd_2O_3 had total pore area 28.39 and 21.79 m^2/g respectively. The pore surface area of the catalysts determined by mercury porosimetry are found to be very low when compared to surface area obtained by BET method. In mercury porosimetry pore area above 20Å was determined. Since there is large difference in the surface area values in mercury porosimetry the pores below 20Å are not taken in to consideration. This indicates a bimodal pore size distribution one above 20Å and one below 20Å, for these binary oxides precipitated at a final pH 10. Aluminas precipitated at the above pH was observed to have a bimodal pore size distribution[141].

2.11.3 Effect of Method of Preparation on Crystallinity

The XRD pattern of all catalysts are shown in Figs. 5 and 5'. Pure $Al(OH)_3$ precipitated and calcined at 400°C shows highly amorphous nature probably because the decomposition is not complete and also because of residual micro porosities. On the other hand the hydrated yttrium oxide is a purely crystalline precipitate. When heated at 400°C it has well defined pattern. Other single oxides like

Eu_2O_3, Al_2O_3 and Y_2O_3 also show diffraction lines as indicated in the Fig. 5. The XRD of binary oxides do not show any diffraction pattern indicating its amorphous nature. All the binary oxides still retain their fine nature and this low temperature calcination at 400°C may not be sufficient for particle coarsening and it may require still higher temperature. This is clearly evident in the thermogravimetric data also. In the case of binry oxides studied, the rare earth oxides shift the decomposition temperatures to lower ranges, still incomplete dehydroxylation takes place.

Even though there is difference in the pH for the precipitation of rare earths and alumina the absence of Al_2O_3 crystallites and rare earth oxide crystallites indicated by XRD shows that the binary metal oxides are not mechanical mixtures but consists of new complex oxides. This could be in the form of metal-o-metal type of linkages.

2.11.4. Thermogravimetric Analysis

Fig. 8 presents the thermogravimetric curves of alumina-rare earth oxides (1:1 mixtures) like Al_2O_3-Y_2O_3, Al_2O_3-Pr_6O_{11}, Al_2O_3-Sm_2O_3, Al_2O_3-Eu_2O_3 and Al_2O_3-Nd_2O_3. Although there is a general tendency seen to bring down the final decomposition temperture to about 550°C, there are differences with respect to the individual rare earth oxides, while Pr_6O_{11}, Sm_2O_3 and Eu_2O_3 influence the major

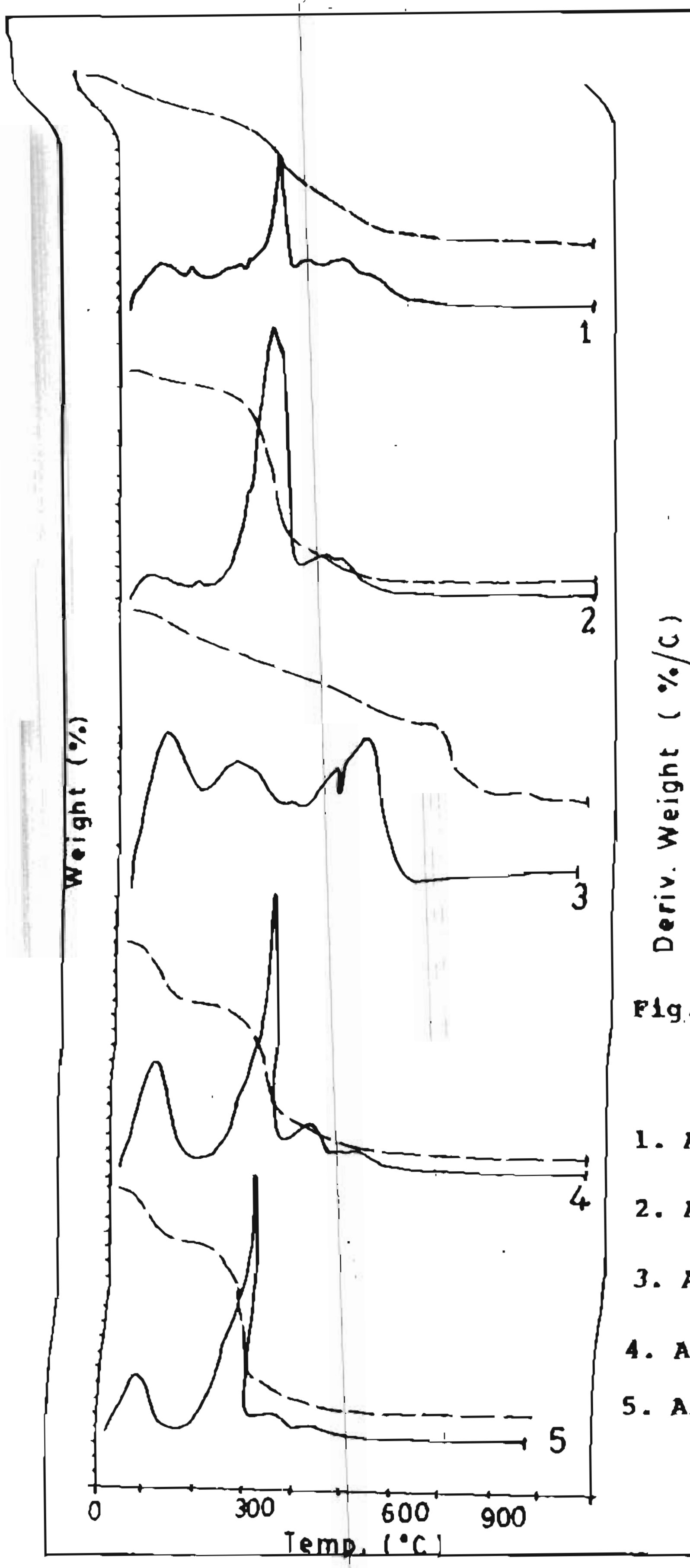


Fig.8. TGA curves for different catalysts

1. Al_2O_3-Y_2O_3

2. Al_2O_3-Pr_6O_{11}

3. Al_2O_3-Nd_2O_3

4. Al_2O_3-Sm_2O_3

5. Al_2O_3-Eu_2O_3

decomposition peak such that the decomposition takes place between 286°C and 296°C.

In the case of Al_2O_3-Pr_6O_{11} the major decomposition takes place at 286.87°C with a mass loss of 38%. Below 400°C 65% of decomposition is complete. For Al_2O_3-Sm_2O_3 there is an initial mass loss of 10% below 100°C followed by a major decomposition at 292.9°C which leaves a residual mass of 51.6%. Al_2O_3-Sm_2O_3 system again shows a small decomposition at 373°C with a residual mass of 72%. Al_2O_3-Y_2O_3 shows an initial decomposition below 100°C followed by a major decomposition at 296°C with a mass loss of 54%. Al_2O_3-Eu_2O_3 system shows a small decomposition at 363°C leaving residual mass 33.5%. For Al_2O_3-Y_2O_3 (1:1) the major decomposition occurs at 298°C with a mass loss of 28% and the system behaves in a different way than the other binary oxides. Further around 70% decomposition takes place much below 400°C in the case of Al_2O_3-Eu_2O_3, Al_2O_3-Pr_6O_{11} and Al_2O_3-Sm_2O_3 suggesting very low extent of free OH groups in these oxides. It is worthwhile to suggest that this decomposition could influence the favourable occurrence of reaction sites in these oxide systems.

Among these three oxides Al_2O_3-Eu_2O_3 (1:1) composition appears to have the lowest loss on ignition much below 400°C suggesting the possibility of higher occurence of reaction sites. Moreover the major decomposition in this

1.11.5 Acidic and Basic Properties

The amount of acid sites at different Hammett acid strengths on unit surface area for the four catalysts are shown in Fig. 9. The acid sites of Al_2O_3-Pr_6O_{11} could not be estimated due to the dull green color of the catalyst. The amount of acid sites at Ho $\leq$ +6.8 was found to be maximum for Al_2O_3-Eu_2O_3 *followed by* Al_2O_3-Nd_2O_3. Al_2O_3-Eu_2O_3 had an acid amount of 0.1135 m mol/m^2 and Al_2O_3-Nd_2O_3 had 0.1074 m mol/m^2 at pKa +6.8. The least acid amount was found for Al_2O_3-Y_2O_3. Same pattern is followed at acid strengths Ho$\leq$+4. At medium acid strength of +3.3 and +1.5, Al_2O_3-Eu_2O_3 showed highest acid amount of 0.035 m mol/m^2 and 0.038m mol/m^2 respectively. At medium acid strength Al_2O_3-Sm_2O_3 was found to have more acid amount than Al_2O_3-Nd_2O_3. At high acid sites of Ho $\leq$ -3, the amount of acid sites is highest for Al_2O_3-Eu_2O_3 followed by Al_2O_3-Sm_2O_3 and least for Al_2O_3-Y_2O_3. It is clear from the acidity values in Table 12 the catalysts have weak to moderate acid strengths.

Al_2O_3 prepared under the same conditions showed more acidities at lower acid strengths than binary oxides. The single oxide catalysts of rare earths showed only weaker acid sites.

All binary oxides of alumina-rare earths showed weaker basic strength ranging in between pKBH values 12.2 to

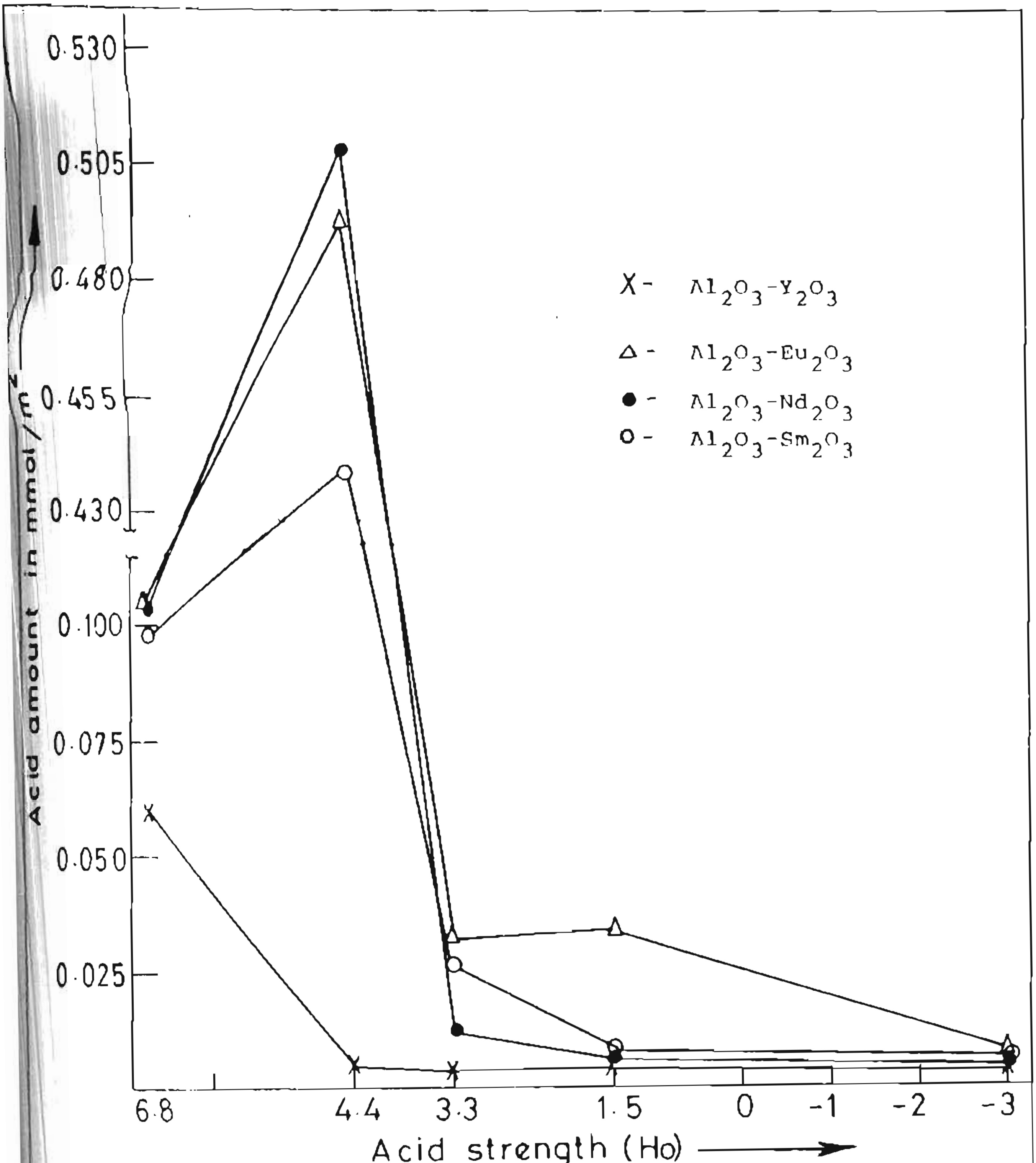


Fig. 9. Acid amount in mmol/m^2 versus acid strength of different catalysts

15. The basic strength and basic amounts of various catalyts are given in Tables 14 and 15. From the table, Al_2O_3-Nd_2O_3 is found to have highest total basicity. Al_2O_3-Eu_2O_3 has got more basic amount at higher sites (15.0) with a value of 0.2864 meq/m^2 followed by Al_2O_3-Nd_2O_3 with a value of 0.2551 meq/m^2. Al_2O_3-Sm_2O_3 has intermediate basicity while Al_2O_3-Y_2O_3 has got least basicity. The single oxides of rare earths did not show any color change with any of the basic indicators. Al_2O_3 showed basicity but the basicity value was less than that of all binary oxides excluding Al_2O_3-Y_2O_3.

Catalytic activities largely depend on the amount and strength of acidic and basic centers on the catalyst surface. Al_2O_3-Eu_2O_3 and Al_2O_3-Y_2O_3 although had same values of surface areas their activities are largely different. This is quite conclusive from the largely different values of the acidity and basicities.

2.11.6 XPS

Information on the basic strength of the mixed oxide catalysts can be obtained from XPS analysis, since XPS data is indicative of site strength$^{146\text{ to }151}$. The electron pair donating ability of the oxides can be correlated to O IS binding energy. The O IS binding energy measured for the three oxides viz. Al_2O_3-Nd_2O_3, Al_2O_3-Pr_6O_{11} and Al_2O_3-Eu_2O_3 are 536, 539.25 and 540eV respectively. The order of basic strength obtained from XPS data is Al_2O_3-Nd_2O_3 > Al_2O_3-Pr_6O_{11} > Al_2O_3-Eu_2O_3, eventhough the difference in binding energy are very small.

2.11.7 Effect of Coprecipitation on Acidic and Basic Properties of Binary Oxide Catalyst when compared to Single Oxide Catalysts.

The single oxide catalysts of rare earths showed acidic sites at weaker acid strengths ranging between +3.3 to +1.5. Al_2O_3 showed acid strengths in between $Ho \leq +1.5$ to $Ho \leq -5.6$. The binary oxides showed an acidity range from $Ho \leq -5.6$ to $Ho \leq -8.1$ showing that there is an increase in the acid strengths of binary oxides when compared to single oxides. Alumina showed more acidity at all acid strengths upto $Ho \leq +1.5$ and showed no acidity at $Ho \leq -3$. But all binary oxides showed acidity in the range from $Ho \leq +6.8$ to $Ho \leq -3$. The increase in acidity at higher acid strength can be accounted by the formation of more strained sites on catalyst surface due to coprecipitation.

The binary oxides studied was found to be weaker bases since they do not show any basic sites at higher basic strengths of H_{-} 18.4 to 26.5. The single oxides of rare earths prepared by the same procedure did not show any basic sites at all, where as Al_2O_3 show basicity less than the binary oxides. There is definitely an increase in basic strength of the mixed oxide catalyst indicating generation of more basic sites than the individual oxides. The thermogravimetric curves indicate that the calcination of the rare earth hydroxide to the oxide is not complete as it shows a peak at 500°C, where as the catalysts were prepared at 400°C. This could also provide an enhancement in the basicity of binary oxide catalysts. The binary oxide catalysts showed higher acidity at higher acid strength and less at lower strength. Binary oxides show more basicity and more basic amount than single oxides. Most probably it could be due to the formation of metal-o-metal bonds formed during calcination from complex hydroxides produced during coprecipitation.

2.11.8. Nature of Coordination of Aluminium Atoms on the Activity of Catalysts

It is reported in the literature that the coordination number of aluminium atoms in the lattice could be inferred from MAS ^{27}AlNMR[142,143,144]. The chemical shift around 60 ppm has been attributed for Al atom in tetrahedral coordination where as for octahedral coordination of aluminium, chemical shift will be between zero to 10 ppm. Table 16 gives the chemical shift value of Al atoms in different catalysts. In the case of Al_2O_3-Y_2O_3, the MAS ^{27}Al NMR spectrum showed two signals one at 69 ppm and other at 7.7 ppm showing both tetrahedral and octahedral coordination. From calculating the percentage areas of the signal at 60 ppm it is found that 1/3rd of the Al atoms are in tetrahedral coordination. In the case of Al_2O_3-Sm_2O_3 two signals are observed, one at 7 ppm and other 62 ppm. From calcualted area percentage it was observed that as in the case of Al_2O_3-Y_2O_3, 1/3rd of Al atoms are present in the tetrahedral coordination. For Al_2O_3-Nd_2O_3 both signals at 56 ppm and 4.3 ppm were having almost equal area indicating that the Aluminium atoms are equally distributed in tetrahedral and octahedral coordinations. For Al_2O_3-Eu_2O_3, Al_2O_3-Pr_6O_{11} very broad signals are obtained. This can be attributed to magnetic anisotropy and quadrapolar interactions of aluminium with rare earth atoms. In the case of Al_2O_3-Eu_2O_3 two signals were obtained at 56.8 ppm and 2.8 ppm. For Al_2O_3-Pr_6O_{11} the signals obtained were at 50 ppm and 4.4 ppm. In both these catalysts both signals are of equal intensity showing that aluminium atoms are present equally in tetrahedral and octahedral coordination.

Table 16

Chemical Shift Values of Various Catalysts in MAS ^{27}AINMR

Catalyst	tetrahedral ppm	octahedral ppm
Al_2O_3-Y_2O_3	69	7.7
Al_2O_3-Pr_6O_{11}	50	4.4
Al_2O_3-Sm_2O_3	62	7
Al_2O_3-Nd_2O_3	56	4.3
Al_2O_3-Eu_2O_3	56.8	2.8

CHAPTER - III

TRANSFORMATION OF TERPENYL OXIRANES OVER BINARY OXIDE CATALYSTS OF ALUMINA - RARE EARTH OXIDES

3.1 Introduction

Terpenyl oxiranes are important intermediates in the functionalization of cheap raw materials like terpene hydrocarbons which are abundantly available from natural essential oils. Many of the hydrocarbons like limonene, pinene etc. are available as optical isomers in nature. Many of the aroma and flavour compounds of commercial importance do have chiral centers in the molecule. The prime example in the odour characteristics of optical isomers is carvone. (-) Carvone has a spear-mint odour, (+) carvone has got a floral odour.

In our ongoing efforts to obtain aroma and flavour compounds of value it was decided to carry out transformation reactions of terpenyl oxiranes using the binary oxide catalysts of alumina-rare earth oxides. The preparation and characterisation of binary oxide catalysts are already described in chapter II. The terpenyl oxiranes used in this study are α-and β-pinene oxides, (+) and (-) limonene oxides, 3-carene oxide and ar-curcumene oxide.

(+) and (-) carvone, myrtenal, nuciferol are very high value aroma compounds used in perfumery industry in large amounts. The terpenyl oxiranes selected for the study could give *the above mentioned high value products.*

The reactivity and selectivity of binary oxide catalysts in the transformation of each terpenyl oxiranes has been dealt with separately. Acidity and basicity of catalysts are determined by surface area, pore size and thermal treatment. Most of the catalytic reactions takes place due to the active participation of the acidic and basic sites present on the surface of the catalyst. The products formed in the heterogeneous catalysis reaction are mainly correlated to acidic and basic strength of the catalyst. Hence it is very essential to have the data for ready reference.

Tables 11, 12 and Fig. 9 give the relevant data about acidity and Tables 14 and 15 give data about the basicity.

Table 11

Acid Strength of Various Binary Oxide Catalysts

Catalyst	Ho range
Al_2O_3-Y_2O_3	-5.6 to -8.1
Al_2O_3-Sm_2O_3	-5.6 to -8.1
Al_2O_3-Eu_2O_3	-5.6 to -8.1
Al_2O_3-Nd_2O_3	-5.6 to -8.1

Table 12

Acidity Distribution of Binary Oxide Catalyst in m mol/m^2 at Various Acid Strength

Catalyst	+6.8	+4	+3.3	+1.5	-3
Al_2O_3-Y_2O_3	0.0589	0.0044	0.0021	0.0030	0.0001
Al_2O_3-Nd_2O_3	0.1074	0.5099	0.0123	0.0070	0.0028
Al_2O_3-Sm_2O_3	0.0924	0.4375	0.0292	0.0041	0.0071
Al_2O_3-Eu_2O_3	0.1135	0.499	0.0350	0.0380	0.0088

Table 14

Basic Strength of Various Binary Oxide Catalysts

Catalyst	H- range
Al_2O_3-Y_2O_3	15 to 18.4
Al_2O_3-Nd_2O_3	15 to 18.4
Al_2O_3-Sm_2O_3	15 to 18.4
Al_2O_3-Eu_2O_3	15 to 18.4

Table 15

Basicity Distribution of Binary Oxide Catalysts in meq/m^2

Catalyst	Basic amount in meq/m^2 in H_- range		
	12.2	15	Total basicity
Al_2O_3-Y_2O_3	0.0243	0.0451	0.0694
Al_2O_3-Nd_2O_3	0.1234	0.2551	0.3785
Al_2O_3-Sm_2O_3	0.1232	0.1335	0.2567
Al_2O_3-Eu_2O_3	0.0592	0.2864	0.3456

3.2 Epoxide Rearrangements

Acidic and basic catalysts like BF_3, $MgBr_2$-t-Buok or lithium dialkyl amide have been frequently used in the catalytic rearrangement of epoxides. With acidic catalysts epoxides generally rearrange to carbonyl compounds and with basic catalysts to allylic alcohols. Recently heterogeneous catalysts like alumina, silica and other solid acid base catalysts were used for epoxide isomerization.

Oxirane ring

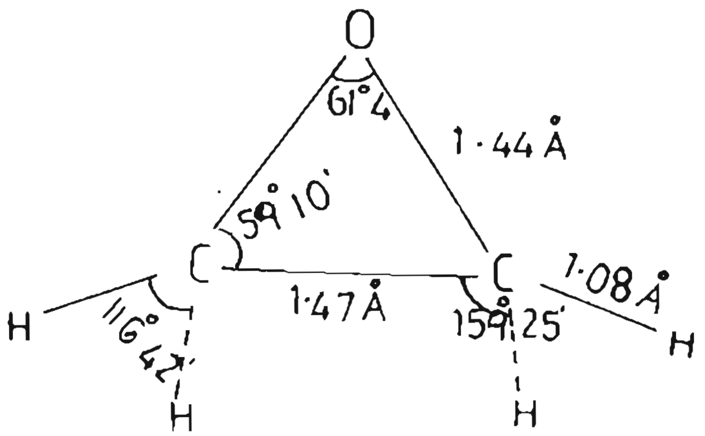


Fig.12. Oxirane ring in ethylene oxide.

samples. Linalyl acetate was chosen as the internal standard in most cases.

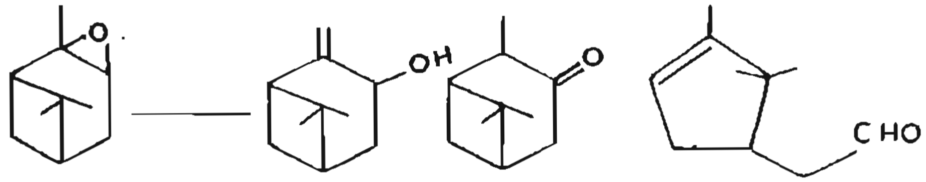
GLC analysis was done on a 5840A Hewlett-Packard gas chromatograph. Column ov17(10%); 1.8 M length, I.D 3.1 mm; carrier gas N_2 at a flow rate 20 ml/min, F.I.D. detector; column temperature programme from 80 to 200°C at the rate of 10°C/min. Injector temperature 250°C, F.I.D. temperature 300°C.

GC-MS was carried out on a Varion - 3400 Incos.50 mass spectrometer. Column DB-5; length 30 M; 1.D 2.5 nm; column temperature programme from 60 to 200°C at the rate of 5°C/min, carrier gas used was helium.

3.3 Transformation of α-Pinene Oxide (2,7,7-Trimethyl-3-oxa tricylo [4.1.1.0] octane)

Earlier Studies

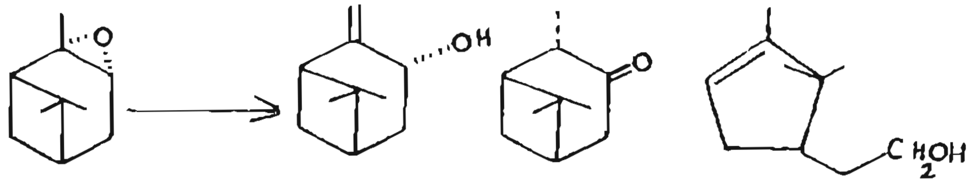
When Nigam and Levi chromatographed[85] α-pinene oxide (9) over active Al_2O_3, pinocarveol (10), cis and trans pinocamphone(11) and α-campholenic aldehyde(12) were obtained.



9 10 11 12

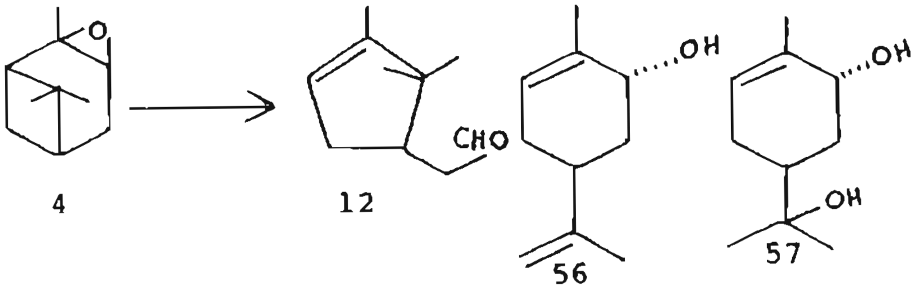
Joshi and co-workers observed the transformation of 2α,3α

-epoxypinane to trans-pinocarveol (20), pinocamphone (11) and α-campholenic alcohol (21) over Al_2O_3[88].



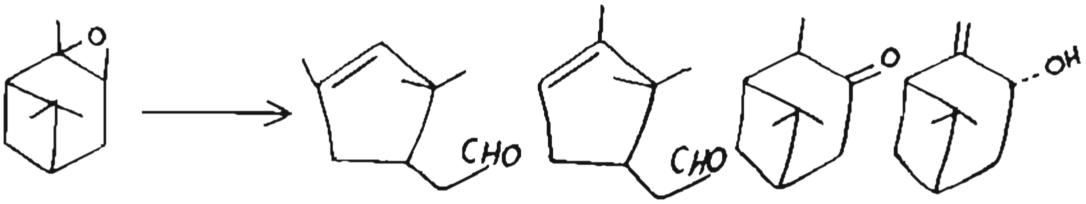
9 20 11 21

Rykowski[107] et al. observed the selective formation of trans-pinocarveol from epoxide in basic media like t-Buok in pyridine or N,N-dimethyl formamide over homogeneous catalysts. Over silica gel Joshi and co-workers observed the formation of large amount of 2,2,3-trimethyl-3 cyclo penten-1-acetaldehyde (12) from α-pinene oxide[89]



4 12 56 57

However in acidic media with BF_3-etherate, $ZnBr_2$ and P-toluene sulphonic acid, epoxide is transformed to α-campholenic aldehyde[110-113]. Tanabe and his co-workers studied the isomerization reactions of α-pinene oxide over a number of solid acid base catalysts like SiO_2-Al_2O_3, SiO_2-TiO_2, solid H_3PO_4, TiO_2, Al_2O_3, $FeSO_4$ etc.[114]. The main products were 2,2,4-trimethyl-3-cyclopenten-1-acetaldehyde (58). α-campholenic aldehyde (12) pinocamphone (11) and trans-pinocarveol(10).



4 58 12 11 10

Pyrolysis of α-pinene oxide on iron catalyst yielded pinocamphone^{112}. Decomposition reactions of α-pinene oxide over synthetic zeolites (like 3A, 4A, 13X and TSZ-645-PSH) were studied by Nomura and co-workers^{155b}. They observed the formation of campholenic aldehyde from α-pinene oxide. α-pinene oxide isomerized to campholenic aldehyde and dihydro carvone over chromic acid adsorbed alumina^{156}.

However a systematic study of the isomerization of α-pinene oxide using alumina - rare earth oxides were not made so far. So we made an attempt in the present work to carry out reactions of α-pinene oxide over Al_2O_3-Y_2O_3, Al_2O_3-Sm_2O_3, Al_2O_3-Pr_6O_{11}, Al_2O_3-Nd_2O_3 and Al_2O_3-Eu_2O_3.

3.3.1 Materials

(+) -pinene (97% pure) supplied by Aldrich Chemical Company, U.S.A. $CaCl_2$ lumps supplied by B.D.H. Solvents, benzene toluene and xylene, ether, 30% H_2O_2 (solution),

3.3.4 Preparation of α-Pinene Oxide

α-pinene oxide was prepared by the method of Royals and Harrell[96]. 100 g of (+)- α-pinene (0.07 mol) was added dropwise to ice cold solution of monoperphthalic acid and the reaction mixture was kept in a refrigerator until the reaction was complete. Rate of the reaction was monitored by TLC. The reaction mixture was extracted with ether. Ethereal solution was washed with aqueous sodium carbonate solution to remove free acid. The solution was separated from the aqueous phase and dried over anhydrous sodium sulphate. The solvent was removed under vacuum. The crude mixture was fractionally distilled in vacuum. The fraction collected at 100-102°C (10 mm Hg) yielded 73 g. Purity of the fraction was found to be 97% by GLC analysis. It is assumed to be a mixture of cis and trans epoxides.

3.3.5 Reactions of α-Pinene Oxide

Reactions at 80°C

α-Pinene oxide (1.3 m mol) and 1 g Al_2O_3-Y_2O_3 and 5 ml benzene were refluxed with stirring. Reaction course was monitored by TLC at 1 hr intervals. After 15 hr the reaction was found to be slow, reaction mixture filtered and catalyst separated. Catalyst was extracted with methylene chloride. All extracts were combined together and solvent removed.

The same procedure was repeated for reactions at 110°C and 140°C. Solvents used were toluene and xylene. Reaction time was 7 hr at 110°C and 6 hr at 140°C. Same reaction procedure was repeated at three different temperatures 80°C, 110°C and 140°C for other binary oxide catalysts, Al_2O_3-Nd_2O_3, Al_2O_3-Pr_6O_{11}, Al_2O_3-Sm_2O_3 and Al_2O_3-Eu_2O_3.

3.3.6 Preparation of Authentic Samples

3.3.6.1 Preparation of Campholenaldehyde (2,2,3-trimethyl -3-cyclopentene-1- acetaldehyde) (12)

Materials

α-pinene oxide, glacial acetic acid (98%), NaoH and anhydrous sodium sulphate supplied by S.D Fine Chemicals Ltd.

Experimental

Campholenaldehyde is prepared by the procedure given by Royals et al[96]. α-pinene oxide (30.4 g, 0.2 mol) was added with stirring to 100 ml glacial acetic acid at 20°C. After the addition reaction mixture was stirred for another 20 hr. 20% NaOH solution added to neutralize the acid at 15°C and the resulting mixture was extracted with ether. Ether extract was washed with water, dried over anhydrous sodium sulphate and solvent removed. The crude mixture was distilled and fraction collected at 55°C (4 mm of Hg) yielded 6 g (20%). Purity of the product was found to be 85% by GLC analysis.

3.3.6.2 Preparation of Pinocarveol(6,6-Dimethyl-2-methylene bycyclo [3.1.1] heptan-3-01) (10)

Materials

SeO_2, Absolute alcohol (supplied by S.D Fine Chemicals) and β-Pinene (supplied by Aldrich Chemical Company, U.S.A)

Experimental

The procedure followed was given by Quinn[157]. About 0.05 mol (6.56 g) of SeO_2 in 30 ml absolute alcohol was added dropwise during 1 hr period, with vigorous stirring to 13.6 g (0.1 mol) of β-pinene. During the addition solution become warm and turned yellow. After stirring another half an hour at room temperature, the solution was refluxed for 4 hour. The reddish brown solution obtained was washed with two-fold quantity of water. The reddish brown solution was filtered to remove the black precipitate of selenium. The solvent removed and solution fractionally distilled and first fraction collected at 70°C (5 mm of Hg) yielded 3.7 g (77%). Purity of pinocarveol was checked by GLC and found to be 87%.

Experimental

The procedure followed was Quinn's method[157]. β-pinene 13.6 g (0.1 mol) was taken in 28 ml of absolute alcohol and 6.56 g (0.05 mol) of SeO_2 powder was slowly added to it during 1 hr period with vigorous stirring. After the addition solution was stirred for another 30 minutes at room temperature. The reaction mixture was then refluxed for 6 to 8 hr. The reddish brown solution obtained at the end of reaction was washed with 75 ml of water. The reaction mixture was separated from aqueous layer. The black precipitate of selenium in the reaction mixture was removed by filteration. Solvent removed and reaction mixture purified by column chromatography on neutral alumina. *Solvent used was 5% methylene chloride in hexane.* The second fraction containing the ketone was separated and solvent removed. The product obtained yielded 3.5 g (25.7%). Purity of the product was checked by GLC and found to be 87%.

3.3.7 Identification of Products

The reaction mixture was analysed by GLC, GC-MS and constituents were identified by comparing relative retention time with authentic samples. MS data given in each case is in the decreasing order of abundance.

Compound 12 was identified as 2,2,3-trimethyl -cyclopentene-1-acetaldehyde by RRT and MS.

108(100), 93,41,67,95,43,55,91.

Compound 10 was identified as isopinocarveol by RRT and MS.

41(100), 55, 91, 70, 79, 119, 105, 134.

Compound 59 was identified as pinocamphol by its RRT and MS.

41(100), 55, 69, 83, 95, 91, 110.

Compound 60 was identified as pinocarvone by its RRT and MS.

81(100), 55, 108, 41, 150, 135, 122, 69, 39, 27.

Compound 70 was identified as cis-myrtanol by its RRT and MS

41(100), 54, 82, 95, 67, 91, 109.

Compound 62 was identified as pinane diol by RRT and MS.

41(100), 95, 109, 53, 91, 67, 43, 55, 77, 93.

Compound 63 was identified as trans-myrtanol by RRT and MS.

41(100), 54, 82, 93, 44, 51, 79, 77, 95, 91, 108.

3.3.8 Results and Discussion

For reaction at 80°C, percentage conversion ranged from 50 to 83 over various binary oxide catalysts. Al_2O_3-Nd_2O_3 showed maximum conversion (83%) to products. Al_2O_3-Sm_2O_3 yielded 82% products. Al_2O_3-Y_2O_3 showed least conversion to products (50%). Among the products the ring contracted aldehyde (12) was the major one produced over all catalysts.

Table 17

Activity and Selectivity of Various Catalysts in Benzene(15 hr)

Catalyst	Conversion	Product %				
	%	12	10	59	60	70
Al_2O_3-Y_2O_3	50	29	11	14	25	-
Al_2O_3-Sm_2O_3	62	34	16	20	19	-
Al_2O_3-Eu_2O_3	82	35	-	21	23	10
Al_2O_3-Nd_2O_3	83	31	17	21	20	-
Al_2O_3-Pr_6O_{11}	65	40	17	16	15	-

Table 18

Activity and Selectivity of Various Catalysts in Toluene (7 hr)

Catalyst	Conversion	Product %					
	%	12	10	59	60	70	62
Al_2O_3-Y_2O_3	80	20	10	20	4	4	4
Al_2O_3-Sm_2O_3	90	18	26	18	19	3	-
Al_2O_3-Eu_2O_3	94	31	11	21	17	6	-
Al_2O_3-Nd_2O_3	91	25	16	20	14	5	-
Al_2O_3-Pr_6O_{11}	93	21	15	17	13	5	7

Table 19

Activity and Slectivity of Catalysts in Xylene (6 hr)

Catalyst	Conversion	Product %						
	%	12	10	59	60	70	62	63
Al_2O_3-Y_2O_3	97	20	10	13	15	-	-	-
Al_2O_3-Sm_2O_3	96	18	22	16	17	-	6	-
Al_2O_3-Eu_2O_3	100	46	-	16	12	-	4	6
Al_2O_3-Nd_2O_3	100	20	12	20	22	-	-	4
Al_2O_3-Pr_6O_{11}	97	29	11	18	18	18	3	4

3.3.8.1 2,2,3-Trimethyl 3-cyclopentene-1-acetaldehyde (12)

At 80°C, carbonyl compounds were the major constituents in the product mixture. Among carbonyl compounds aldehyde (12) predominated over ketone (60). At 80°C Al_2O_3-Pr_6O_{11} produced 40% yield of aldehyde, while Al_2O_3-Eu_2O_3 produced 35% yield of aldehyde and Al_2O_3-Sm_2O_3 produced 34%. At 110°C the percentage yield of aldehyde varied from 18 to 31. Al_2O_3-Eu_2O_3 produced 31% yield of aldehyde and Al_2O_3-Nd_2O_3 produced 25% yeild. Lowest yields of 18% and 20% were obtained for Al_2O_3-Sm_2O_3 and Al_2O_3-Y_2O_3.

At 140°C, Al_2O_3-Eu_2O_3 produced 46% aldehyde, Al_2O_3-Pr_6O_{11} produced 29% aldehyde. The yield of aldehyde varied from 18 to 46% over various catalysts. Lowest yield

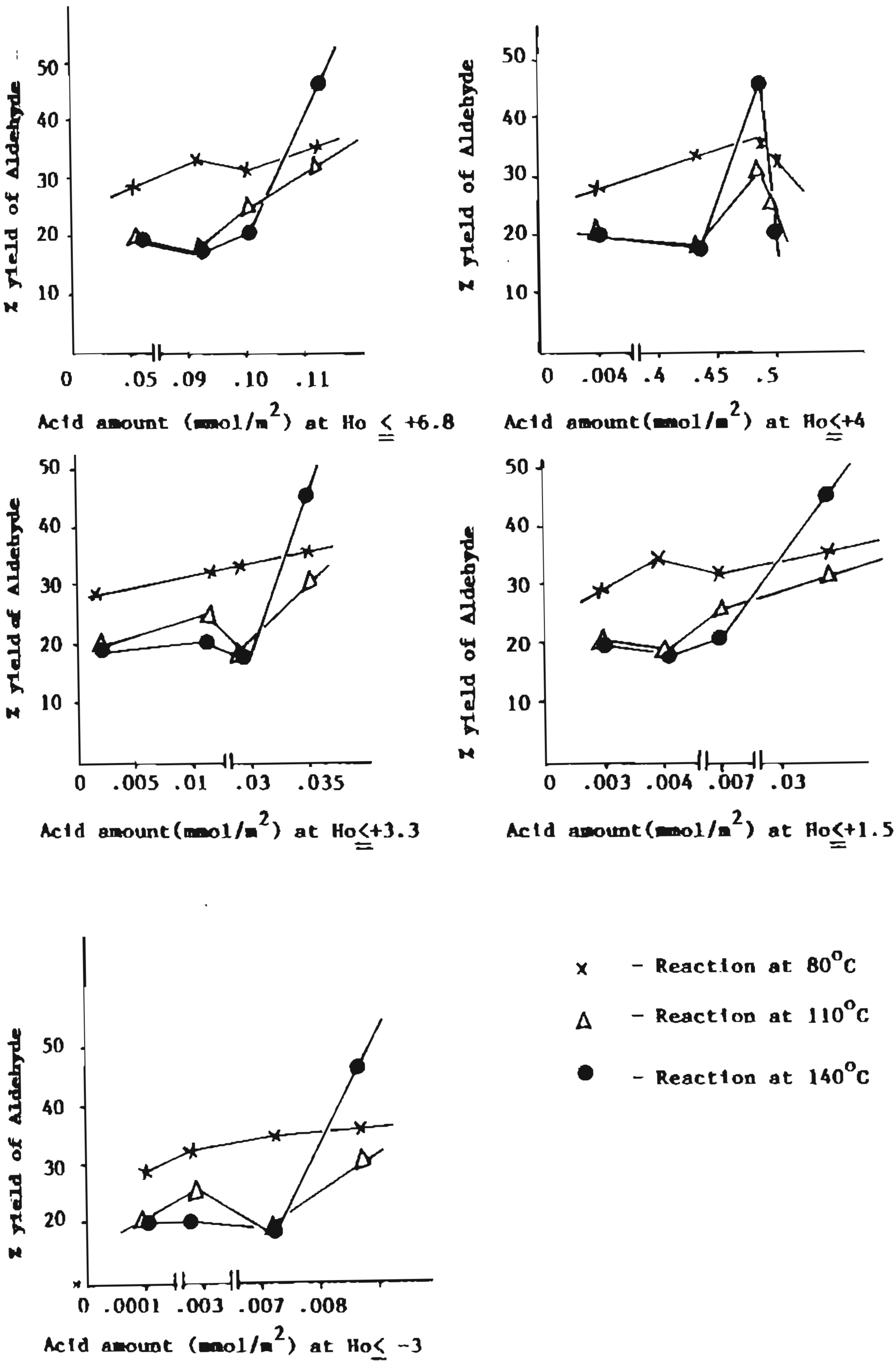


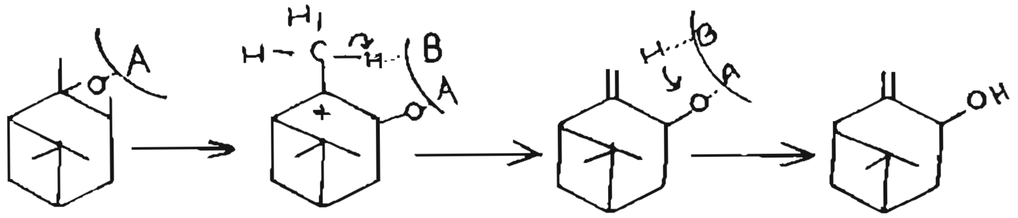
Fig.13 Variation of percentage yield of Aldehyde with acid amount

the results indicate that a lower temperature of 80°C is more favourable for the formation of aldehydes.

3.3.8.2 Trans-pinocarveol(1α,3α,5α)-6,6-dimethyl-2-methylene bicyclo [3.1.1] heptan-3-01) (10)

At 80°C the yield of pinocarveol varied from 11 to 17%. Al_2O_3-Nd_2O_3 and Al_2O_3-Pr_6O_{11} produced maximum yield of 17% and Al_2O_3-Sm_2O_3 produced only 16% yield of carveol. Al_2O_3-Y_2O_3 produced lowest yield (11%) and Al_2O_3-Eu_2O_3 produced no pinocarveol at 80°C. At 110°C Al_2O_3-Sm_2O_3 showed highest yield of 26% while Al_2O_3-Y_2O_3 produced minimum yield (10%). The yield of pinocarveol ranged from 10 to 26% at 110°C. As temperature changed from 80 to 110° the yield of alcohol decreased over all catalysts except Al_2O_3-Sm_2O_3. At 140°C the yield of pinocarveol decreased except in the case of Al_2O_3-Y_2O_3. Al_2O_3-Y_2O_3 yielded 10% alcohol at 110°C and 140°C. At highest temperature 140°C the percentage yield varied from 10 to 22, Al_2O_3-Eu_2O_3 produced no alcohol at 140°C.

The formation of allyl alcohol can be depicted as below. The epoxide gets adsorbed on an acid site on the catalyst surface and epoxide ring opens up forming a tertiary carbonium ion. At the same time a proton from the methyl group is extracted by a basic site adjacent to acidic site which results in an exocyclic double bond. The proton from the basic site attacks the oxygen atom resulting in the formation of alcohol.



A : Acidic site B : Basic site

At lower acid strengths an increase in the percentage yield of allyl alcohol with acid amount was observed. At higher acid amounts there is a decrease in the percentage yield of alcohol for all catalysts. The variation of allyl alcohol production with acid amount in m mol/m^2 is given in Fig 14.

3.3.8.3 Pinocamphol.[(1α,2α,3α,5α)-2,6,6-trimethyl-bicyclo [(3.1.1) heptan-3-01] (59)

The yield of pinocamphol varied from 14 to 21% at 80°C. Al_2O_3-Eu_2O_3 and Al_2O_3-Nd_2O_3 produced alcohol in 21% while Al_2O_3-Sm_2O_3 produced only 20% alcohol. Lowest yield of 14% was observed over Al_2O_3-y_2O_3. At 110°C, the percentage production of pinocamphol varied from 17 to 21%. Al_2O_3-Eu_2O_3 produced maximum yield (21%) while Al_2O_3-Nd_2O_3 produced 20% pinocamphol. No significant variation in the yield of pinocamphol was observed except in the case of Al_2O_3-Y_2O_3 when temperature changed from 80 to 110°C. Al_2O_3-Y_2O_3 produced 20% pinocamphol at 110 $^\circ$C. Al_2O_3-Y_2O_3,

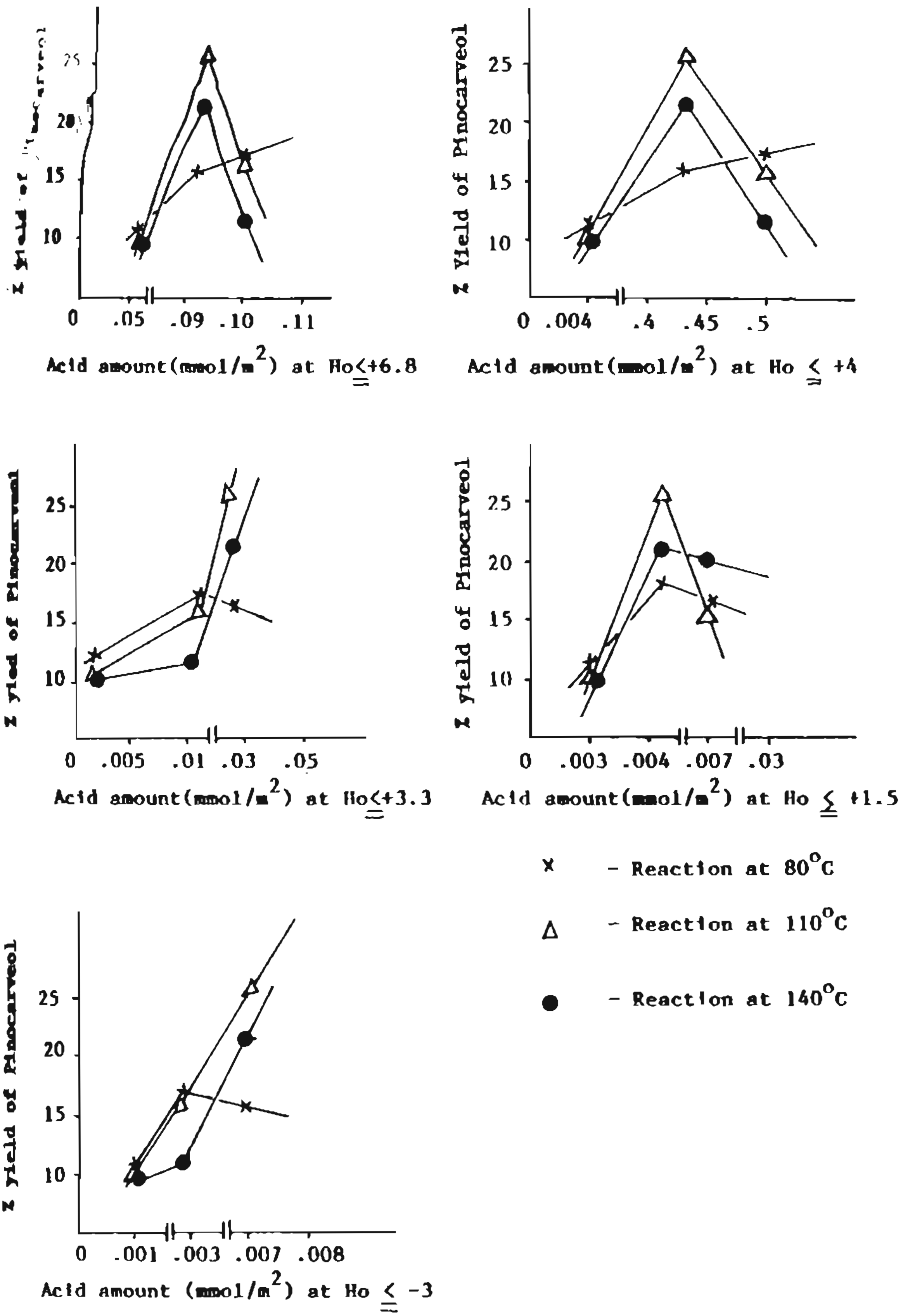
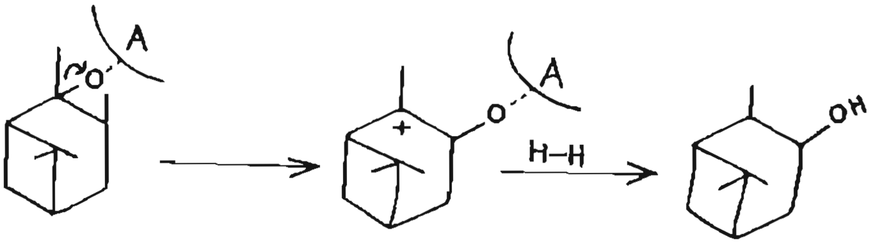


Fig.14 Variation in the yield of Pinocarveol with acid amount

Al_2O_3-Sm_2O_3 and Al_2O_3-Eu_2O_3 showed a decrease in the yield when temperature increased from 110°C to 140°C. Maximum yield was observed over Al_2O_3-Nd_2O_3 (20%) and Al_2O_3-Pr_6O_{11} produced increase in production of pinocamphol at 140°C.

The formation of pinocamphol can be illustrated as follows. The epoxide attaches it self to the surface of the catalyst through oxygen atom. The epoxide ring opens up to form a tertiary carbonium ion which abstracts protons from catalyst surface to form the alcohol.



A; Acidic site

As evident from the *Fig. 15* at 80°C there is a regular increase in the production of pinocamphol with acid amount at Ho $\leq$ +6.8, +4 and +1.5. At other temperatures there is no regular variation in the percentage production with acid amount. An increase in the yield of pinocamphol with basicity at H_15 was also observed.

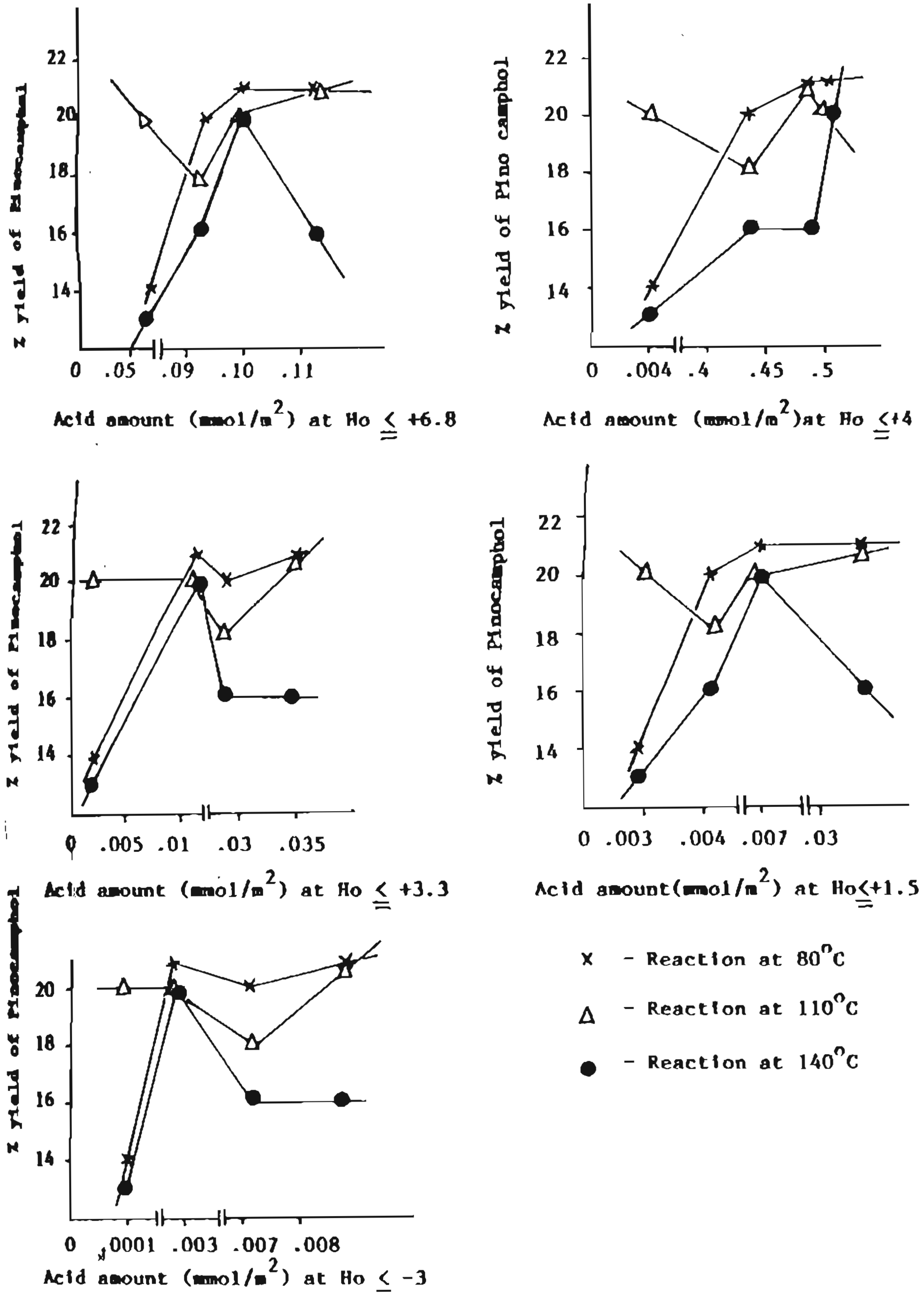
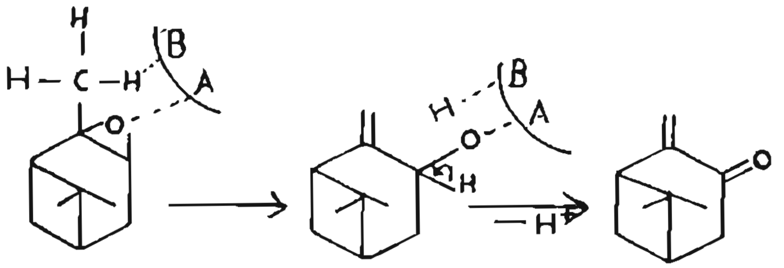


Fig.15 Variation of percentage yield of Pinocamphol with acid amount

3.3.8.4 Pinocarvone (2-Methylene-6,6-dimethyl bicyclo[3.1.1] heptan-3-one) (60)

At 80°C the percentage production of pinocarvone varied from 15 to 25. Highest yield was observed over Al_2O_3-Y_2O_3. Al_2O_3-Eu_2O_3 produced 23% and Al_2O_3-Nd_2O_3 produced 20% pinocarvone. At 110°C the yield of pinocarvone changed from 4 to 19%. Highest yield 19% was observed over Al_2O_3-Sm_2O_3 followed by 17% yield in the case of Al_2O_3-Eu_2O_3. Al_2O_3-Nd_2O_3 produced 14% pinocarvone, and Al_2O_3-Y_2O_3 produced only 4% yield. At 140°C the percentage yield of pinocarvone ranged from 12 to 22%. Al_2O_3-Nd_2O_3 showed 22% conversion, while 18% conversion was observed over Al_2O_3-Pr_6O_{11}. 15% yield of pinocarvone was observed over Al_2O_3-Y_2O_3 and Al_2O_3-Eu_2O_3 showed lowest yield of 12%.

The formation of pinocarvone from epoxide can be illustrated as follows. The epoxide gets adsorbed on an acidic site at catalyst surface through oxygen atom. A proton from the methyl group is abstracted by an adjacent basic site, mean while epoxide ring opens upto form tertiary carbonium ion and an exocyclic double bond is created on the



A - Acidic site

B - Basic site

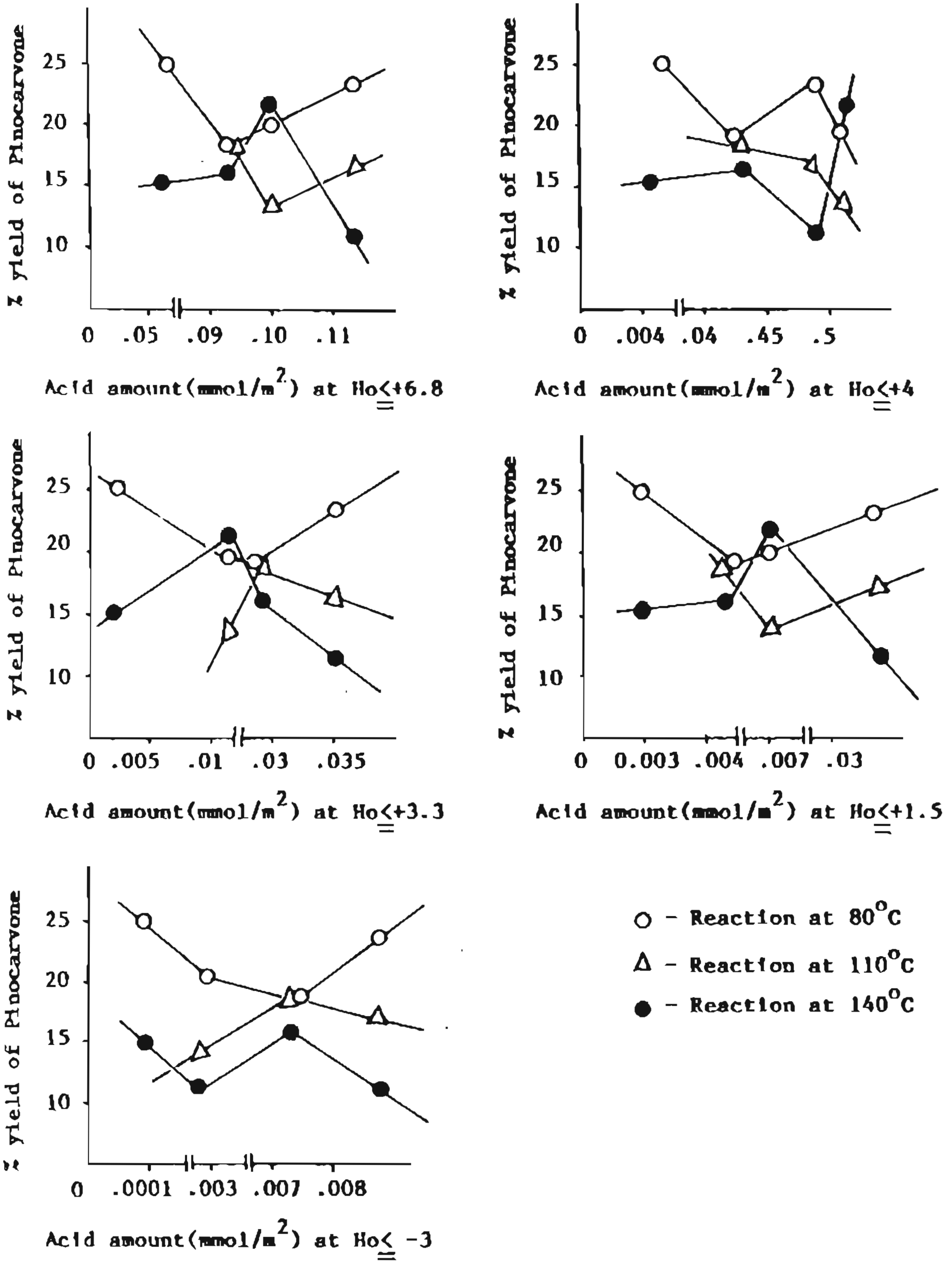


Fig.16 Variation of percentage yield of pinocarvone with acid amount

ring. A proton is eliminated and a carbonyl group is formed which gets desorbed from the catalyst surface.

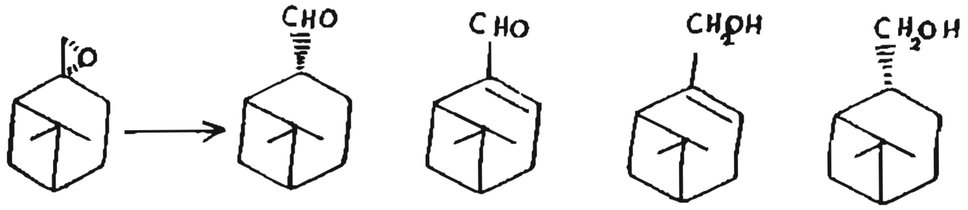
Fig. 16 shows the variation in the yield of pinocarvone with acid amounts of different acid strength. No specific pattern was observed at different temperatures and acid strength hence useful conclusions could not be obtained. A general observation would be that the yield was some what lower at 110°C when compared to that at 80°C and 140°C.

Carbonyl compounds were the major components in the products at 140°C. In these reactions studied a number of compounds were produced in very small amounts which could not be identified. Al_2O_3-Eu_2O_3 produced 10% cis-myrtanol at 80°C while all catalysts except Al_2O_3-Pr_6O_{11} produced cis-myrtanol in 3 to 6% at 110°C. Al_2O_3-Pr_6O_{11} produced cis-myrtanol in 18% at 140°C. Al_2O_3-Eu_2O_3 and Al_2O_3-Pr_6O_{11} produced diol in 4 and 3% yield at 140°C. Trans-myrtanol was produced in 4 and 7% yield by Al_2O_3-Y_2O_3 and Al_2O_3-Pr_6O_{11} at 110°C and at 140°C trans-myrtanol yield varied from 4 to 6% over Al_2O_3-Nd_2O_3 to Al_2O_3-Eu_2O_3.

3.4. Transformations of β-Pinene Oxide [6,6-Dimethyl-tetracyclo (3.1.1.1.1) heptane] (69)]

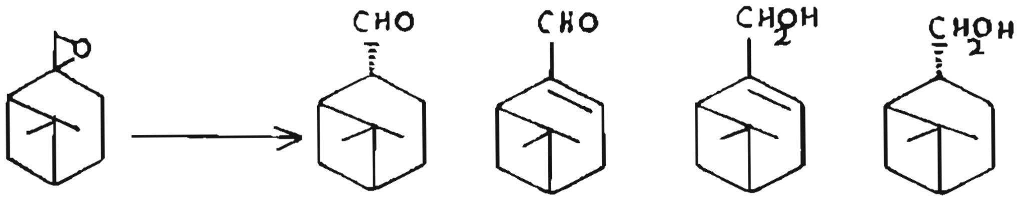
Earlier studies

Sukh Dev and co-workers[155a] studied the effect of modifying the Al_2O_3 with various bases or salts and they observed that with 2,2-disubstituted oxiranes the main products are aldehydes. 2α, 10-Epoxy pinane (64) produced trans-myrtanal (65) and myrtenol (67) in 3:1 ratio and over Al_2O_3-NaOH in hexane at 25°C produced trans-myrtanal (65), myrtenal (66), myrtenol (67) and trans-myrtanol (63).



64 65 66 67 63

2α, 10-Epoxy pinene (68) under the same conditions gave same products over Al_2O_3-NaOH.



68 65 66 67 63

Nomura and co-workers[155b] observed the formation of perillyl alcohol from 2(10)-pinene oxide over synthetic zeolites like 3A, 4A, 13X and TS2-645-PSH in presence of HCOOH.

3.4.1 Materials

β-Pinene oxide (90% pure) supplied by Aldrich Chemical Company, Solvents benzene, toluene and xylene were supplied by E.Merck (India) Ltd are guaranteed reagents which were purified as described before.

3.4.2 Reactions of β-Pinene Oxide

Experimental

Reaction at 80°C

β-Pinene oxide (1.3 m mol) and Al_2O_3-Y_2O_3 (1 g) and 5 ml solvent (benzene) were stirred under reflux. The course of the reaction was monitored by TLC. After 6 hr reaction was found to be very slow. Reaction mixture filtered and catalyst extracted with methylene chloride and filtered. All filtrates combined together and solvent removed in vacuum.

The same procedure was followed for all catalysts and for reactions at 110°C and 140°C. Reactions were monitored at 1 hr intervals by TLC. Reaction time was 6 hr in both cases.

3.4.3 Preparation of Authentic Samples

Preparation of myrtenal - [6,6-Dimethyl bicyclo [3.1.1] hept-2-ene-2-carboxaldehyde] (66).

Materials

Myrtenol (supplied by Sigma Chemie), dry CH_2Cl_2 (supplied by BDH) and pyridinuium chloro chromate (supplied by Aldrich Chemical Company)

Experimental

Myrtenol 2 g (0.013 mol) was taken in 10 ml dry CH_2Cl_2, excess pyridinium chlorochromate (4 g) added to this solution and stirred for 4 hr. It is then extracted with methylene chloride and pyridine removed by washing with excess copper sulphate and dilute HCl. It is then washed with water and solvent removed. Yield obtained 1.1 g (55%). Purity of the product was found to be 78% by GLC analysis.

3.4.4 Identification of Products

The products in the reactions were analysed by GLC and GC-MS and constituents were identified by comparing relative retention times with authentic samples. MS data of all compounds given are in the decreasing order of abundance.

Compound 70 was identified as cis-myrtanol by its RRT and MS.

41(100), 54, 82, 95, 67, 91, 109.

Compound 71 was identified as cis-myrtanal by RRT and MS.

41(100), 79, 55, 67, 86, 123, 59, 114, 105, 133.

Compound 65 was identified as trans-myrtanal by RRT and MS.

79(100), 41, 67, 107, 55, 85, 93, 122, 113, 135, 153.

Compound 66 was identified as myrtenal by its RRT.

Compound 67 was identified as myrtenol by RRT and MS.

79(100), 91, 108, 119, 41, 93, 92, 43, 121, 152.

3.4.5 Results and Discussion

Reactions were carried out at 80°C, 110°C and 140°C. The percentage conversion over various catalyst are illustrated in Fig. 17. Tables 20, 21 and 22 give the activity and selectivity of various catalysts at different temperatures. At 80°C the percentage conversion ranged from 59 to 68. Maximum conversion 68% was observed over Al_2O_3-Sm_2O_3 and Al_2O_3-Nd_2O_3. Al_2O_3-Y_2O_3 and Al_2O_3-Eu_2O_3 produced 63% conversion to products and least conversion 59% was observed over Al_2O_3-Pr_6O_{11}.

Table 20

Activity of Catalysts at 80°C for β-Pinene Oxide Isomerization

Catalyst	Conversion %	Product %				
		70	71	65	66	67
Al_2O_3-Y_2O_3	63	15	4	45	-	7
Al_2O_3-Sm_2O_3	68	24	1	40	6	5
Al_2O_3-Eu_2O_3	63	15	3	51	5	3
Al_2O_3-Nd_2O_3	68	24	2	37	5	6
Al_2O_3-Pr_6O_{11}	59	17	-	38	3	4

Table 21

Activity of Catalysts at 110°C for β-Pinene Oxide Isomerization

Catalyst	Conversion %	Products % 70	71	65	66	67
Al_2O_3-Y_2O_3	50	6	6	10	-	8
Al_2O_3-Sm_2O_3	63	14	-	5	7	5
Al_2O_3-Eu_2O_3	56	29	-	5	9	6
Al_2O_3-Nd_2O_3	53	32	-	4	8	6
Al_2O_3-Pr_6O_{11}	57	24	-	5	5	5

Table 22

Activity of Catalysts at 140° C for β-Pinene Oxide Isomerization

Catalyst	Conversion %	Products % 70	71	65	67
Al_2O_3-Y_2O_3	85	24	9	9	10
Al_2O_3-Sm_2O_3	73	22	6	4	12
Al_2O_3-Eu_2O_3	59	20	7	5	6
Al_2O_3-Nd_2O_3	63	29	4	6	6
Al_2O_3-Pr_6O_{11}	66	30	7	6	4

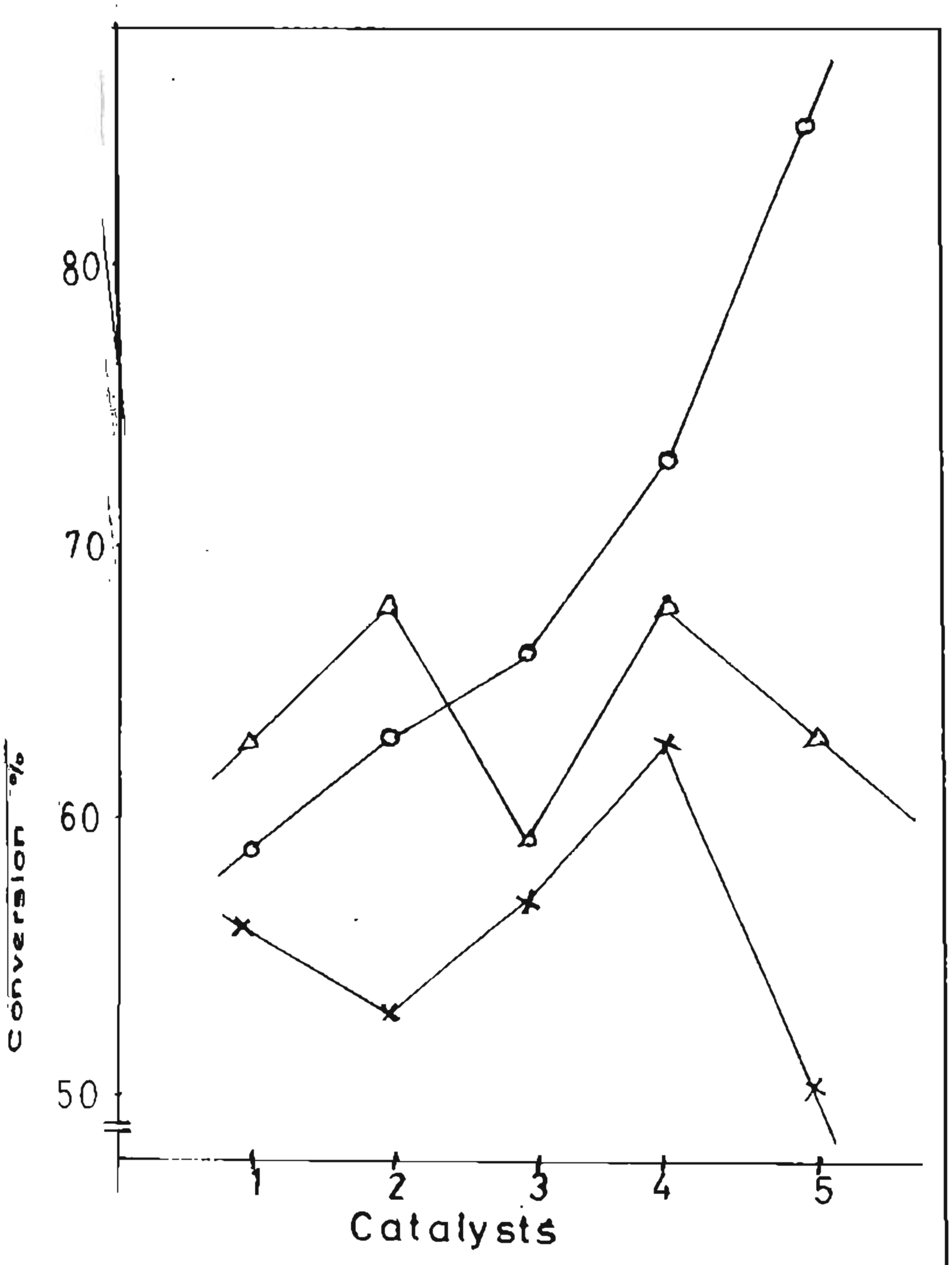


Fig.17 Percentage conversion of β -pinene oxide over various catalysts at different temperatures

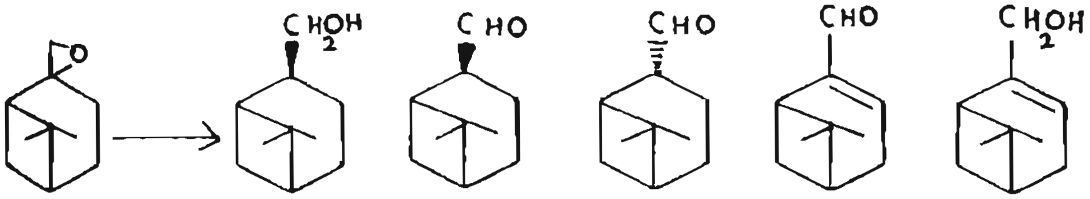
O - Reaction at 140°C ∆-Reaction at 80°C

X - Reaction at 110°C

1. Al_2O_3-Eu_2O_3, 2. Al_2O_3-Nd_2O_3 3. Al_2O_3-Pr_6O_{11}
4. Al_2O_3 -Sm_2O_3 , 5. Al_2O_3 -Y_2O_3

As the reaction temperature changed to 110°, the percentage conversion decreased to the range of 50 to 63 over various catalysts. Al_2O_3-Sm_2O_3 showed maximum conversion 63% to products, while Al_2O_3-Eu_2O_3 and Al_2O_3-Pr_6O_{11} showed conversions of 56 and 57% respectively. At 140°C, Al_2O_3-Y_2O_3 showed maximum reactivity with an yield of 85% followed by Al_2O_3-Sm_2O_3 to Al_2O_3-Nd_2O_3 and Al_2O_3-Pr_6O_{11} produced 63 and 66% conversion to products. Al_2O_3-Eu_2O_3 produced only 59% conversion to products.

Over the five binary oxide catalysts β-pinene oxide was transformed to give *cis and trans-myrtanal (71 and 65)* myrtenal (66), *cis-myrtanol* (70) and myrtenol (67)



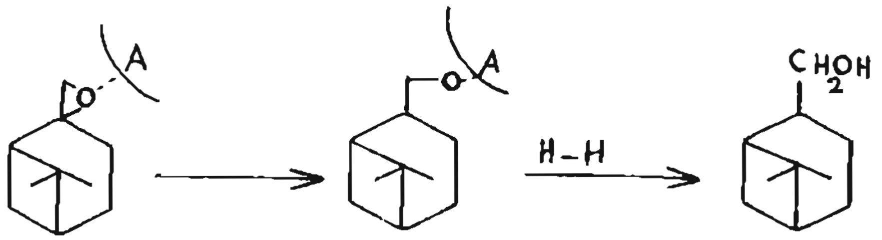
69 70 71 65 66 67

At 80°C carbonyl compounds were the major products formed over various catalysts. At 110°C and 140°C alcohols were major components in product mixture.

3.4.5.1 Cis-myrtanol [Cis-6, 6-dimethyl bicyclo [3.1.1] heptane-2-methanol] (70)

At 80°C the yield of cis-myrtanol varied from 15 to 24%. Al_2O_3-Sm_2O_3 and Al_2O_3-Nd_2O_3 were the best catalysts for the formation of cis-myrtanol with a percentage yield of 24. Al_2O_3-Pr_6O_{11} produced 17% yield of cis-myrtanol, while Al_2O_3-Eu_2O_3 yielded only 15 %. At 110°C, Al_2O_3-Y_2O_3 and Al_2O_3-Sm_2O_3 showed a decrease in yield to 6 and 14%. Al_2O_3-Eu_2O_3 produced an increase in yield to 29% and Al_2O_3-Nd_2O_3 showed much higher yield of 32%. Al_2O_3-Pr_6O_{11} showed a steady increase in yield from 17 to 24 and to 30% when temperature changed from 80 to 110 and to 140°C. At 140°C the yield of cis-myrtanol varied from 20 and 30% over various catalysts. Al_2O_3-Nd_2O_3 produced only 29% yield while Al_2O_3-Y_2O_3 yielded 24% of cis-myrtanol.

The initial step in these reactions is the formation of a tertiary carbonium ion by adsorption of an epoxide oxygen atom on an acid site on catalyst surface. The carbonium ion (B') then abstracts a proton from catalyst surface to give the alcohol.



A: **Acidic site**

Fig. 18 gives the variation in the yield of cis-myrtanol with acidic amount at various Ho values. For reaction at 110°C the yield of cis-myrtanol increased with acid amount at Ho $\leq$ +4 and +1.5. The variation of percentage production

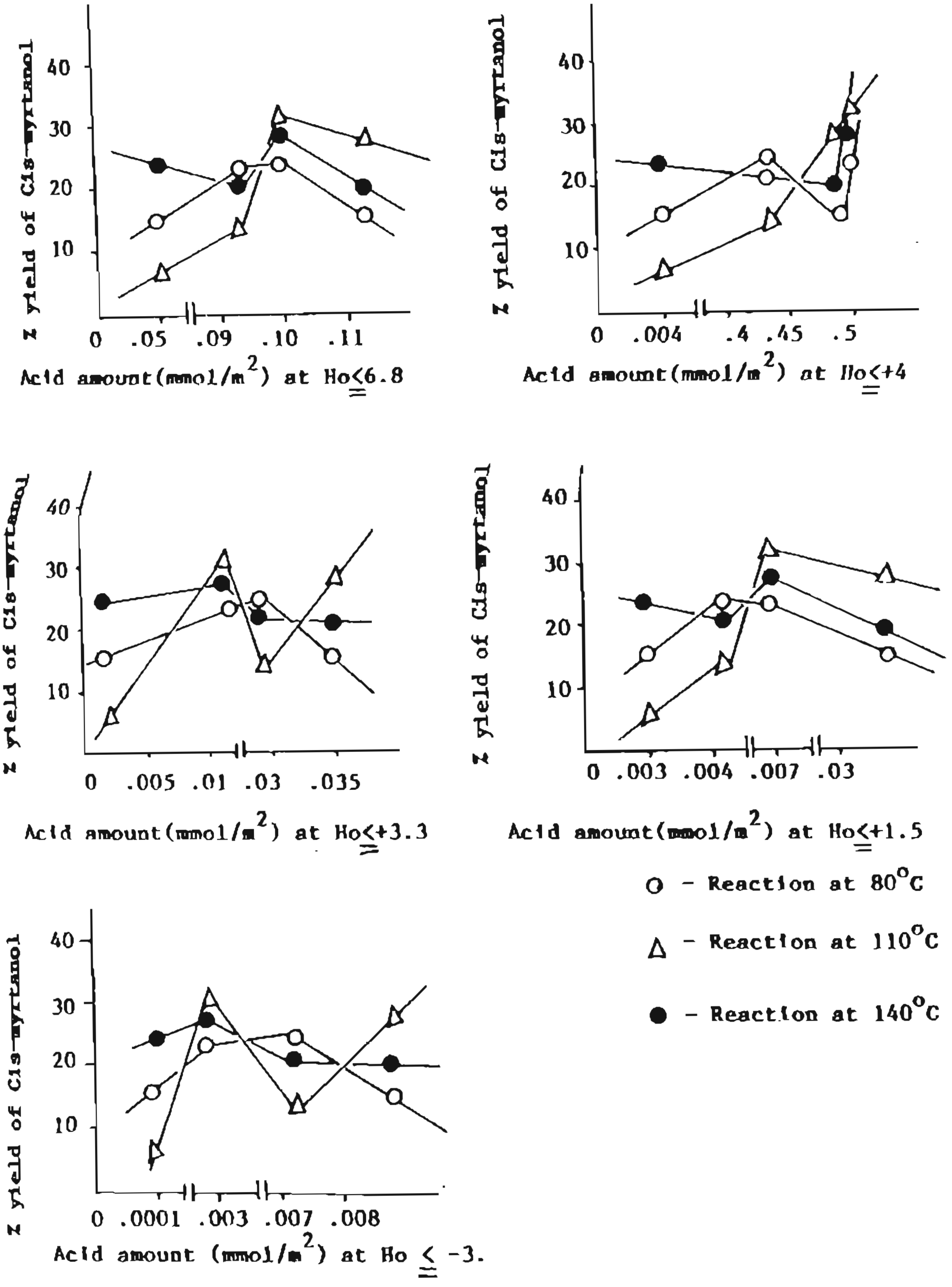


Fig. 18 Variation of percentage yield of Cis-myrtanol with acid amount

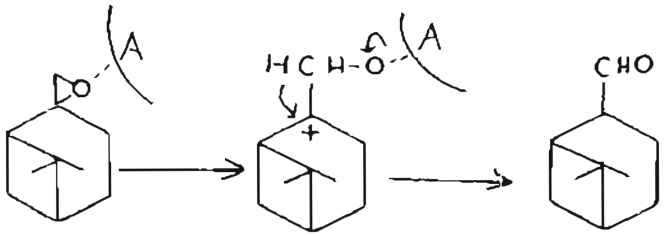
with acid amount is not regular at other temperatures and no correlation can be observed.

3.4.5.2 Trans-myrtanal [Trans-6,6-dimethyl bicyclo [3.1.1] heptane-2 carboxaldehyde] (65)

Trans-myrtanal is the major product formed over various binary oxide catalysts at 80°C and the percentage yield varied from 37 to 51. Al_2O_3-Eu_2O_3 produced maximum yield of 51% followed by Al_2O_3-Y_2O_3 (45%). Al_2O_3-Sm_2O_3 produced 40% yield and Al_2O_3-Pr_6O_{11} produced 38% trans-myrtanal. At 110°C the yield of trans-myrtanal decreased from 4 to 10% over various catalysts. Al_2O_3-Y_2O_3 produced maximum yield of 10% and 5% yield was observed over Al_2O_3-Sm_2O_3 and Al_2O_3-Eu_2O_3. At 140°C the yield varied from 4 to 9% with maximum yield 9% over Al_2O_3-Y_2O_3 and minimum 4% over Al_2O_3-Sm_2O_3. Al_2O_3-Nd_2O_3 and Al_2O_3-Pr_6O_{11} produced 6% yield of trans-myrtanal.

Cis-myrtanal (71) was produced in small amounts of 1 to 4% over various catalysts at 80°C and no catalysts produced cis-myrtanal at 110°C and 140°C with exception of Al_2O_3-Y_2O_3. Al_2O_3-Y_2O_3 produced 6% yield at 110°C.

The initial step in the formation of aldehyde is the adsorption of epoxide on catalyst surface through oxygen atom. The expoxide ring opens up which results in the formation of a tertiary carbonium ion which abstracts a proton from CH_2-O resulting the formation of an aldehyde.



A: Acidic site

The variation in the production of trans-myrtanal with acid amound in m mol/m^2 is depicted in Fig.19. The variation in the yield of trans-myrtanal with acidities is not regular. At various acid strengths, the percentage production decreased with increase in acid amount and then increased with further increase in acid amount.

3.4.5.3 Myrtenal [6,6-Dimethyl bicyclo[3.1.1] hept-2-ene -2-carboxalydehyde] (66)

The percentage yield of myrtenal varied from 3 to 6% at 80°C over various catalysts and a slight increase in yield was observed at 110°C from 5 to 9%. Al_2O_3-Eu_2O_3 produced maximum yield of 9%. Al_2O_3-Nd_2O_3 produced 8% myrtenal and Al_2O_3-Sm_2O_3 produced 7%. At 140°C the yield of myrtenal decreased to a maximum yield of 6% over Al_2O_3-Nd_2O_3 and Al_2O_3-Pr_6O_{11}.

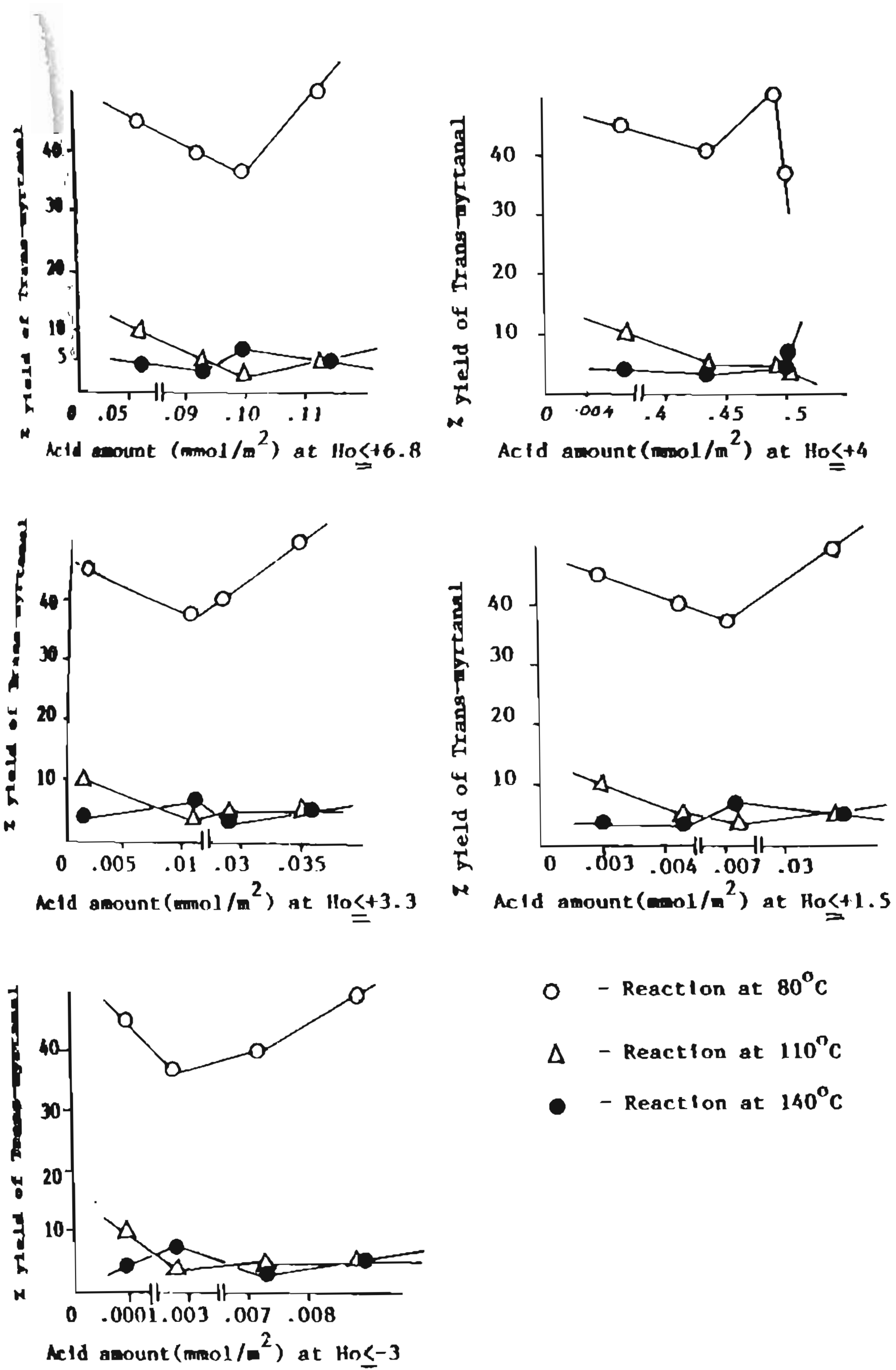
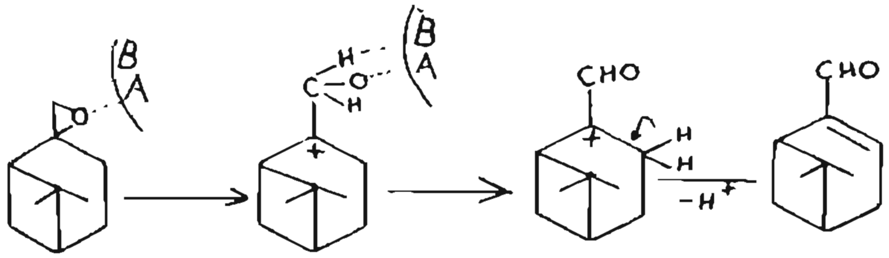


Fig.19 Variation in the percentage yield of Trans-myrtanal with acid amount

The formation of the aldehyde involves the initial formation of carbonium ion by the adsorption of epoxide on catalyst surface, along with the abstraction of a proton from CH_2O-group by a basic site adjacent to acidic site. A proton is eliminated near the tertiary carbon with the formation of an unsaturation in the ring.

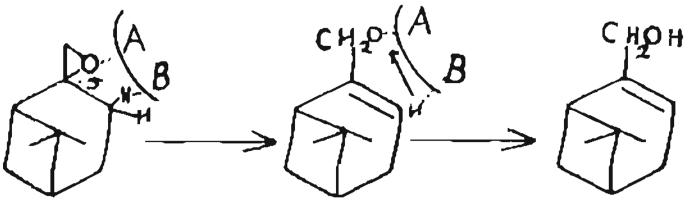


A: Acidic site   B: Basic site

3.4.5.4 Myrtenol [6,6-Dimethyl bicyclo [3.1.1] hept-2-ene -2-methanol] (67)

The yield of myrtenol is small when compared to other products. At 80°C the percentage production of myrtenol varied from 3 to 7 over various catalysts with maximum 7% yield over Al_2O_3-Y_2O_3. At 110°C the yield varied from 5 to 8% with maximum over Al_2O_3-Y_2O_3. At 140°C a slight increase in yield was observed from 4 to 12%. Maximum yield was observed over Al_2O_3-Sm_2O_3 (12%) followed by Al_2O_3-Y_2O_3 (10%).

The first step in the formation of myrtenol is the formation of tertiary carbonium ion and a proton is abstracted from the molecule by a basic site adjacent to acidic site. The proton migrates from basic site to oxygen resulting in the formation of myrtenol.



A : Acidic site B: Basic site

An attempt has been made to correlate the yield of myrtenol with acid amount at various acid strengths. It is illustrated in Fig. 20. The variation in the yield of alcohol with acid strength is irregular. So we could not observe a regular correlation between acidity and yield of myrtenol.

3.4.6 Comparison of Reactivity of α and β-Pinene Oxides

The trialkyl substituted 1,2 epoxide, α-pinene oxide is more reactive than the 2,2 disubstituted oxirane, β-pinene oxide. Reactivity of α-pinene oxide increased with temperature. β-pinene oxide showed a fall in reaction rate from 80 to 110°C and again an increase in reaction rate when temperature changed to 140°C. At 80°C α-pinene oxide yielded carbonyl compounds in 51% to 56%, and yield varied

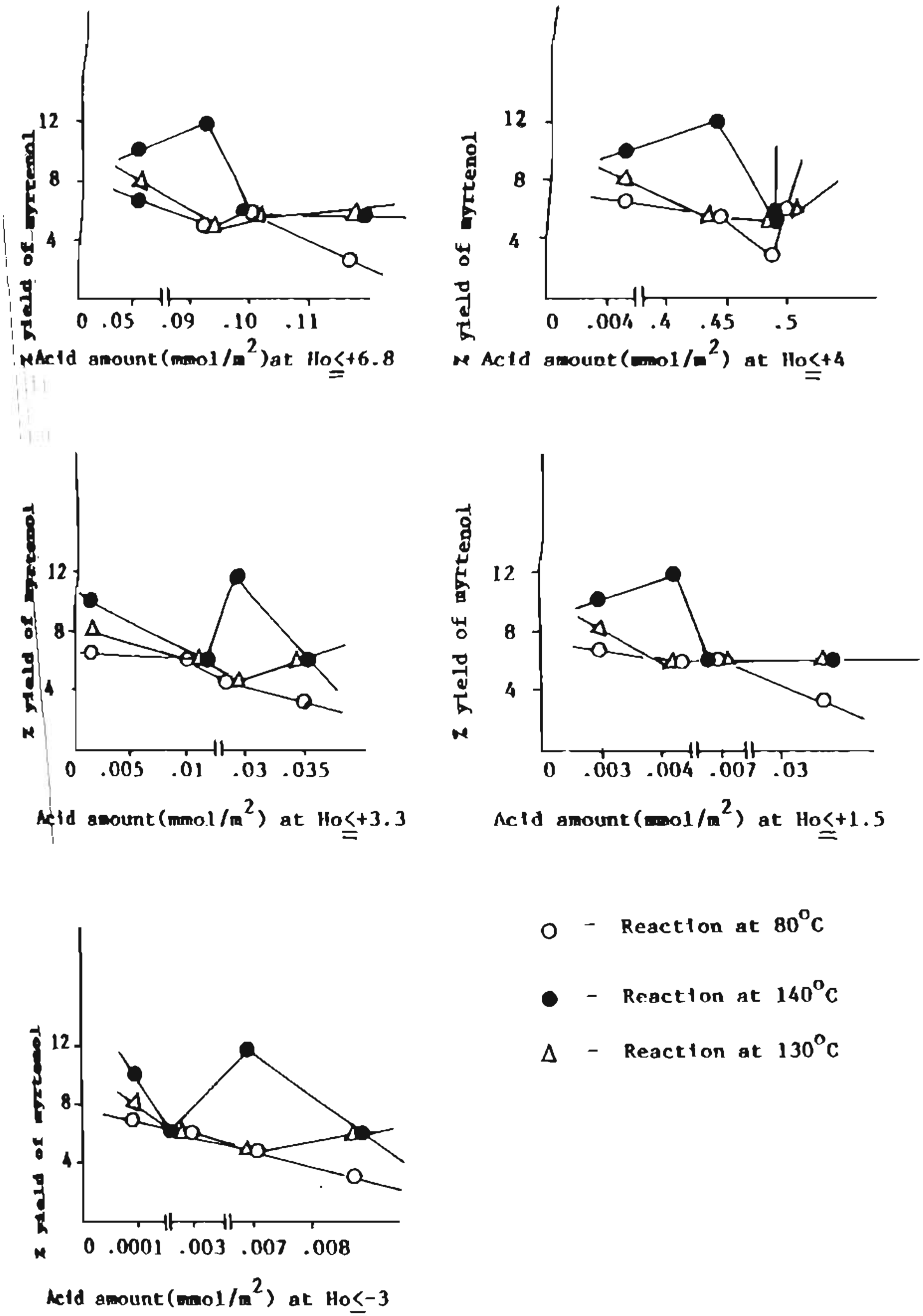


Fig.20 Variation in the percentage productin of Myrtenol with acid amount

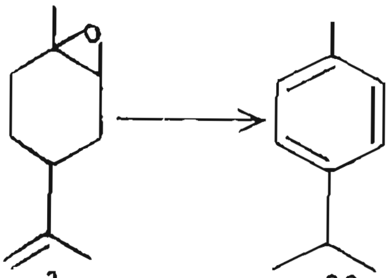
from 35 to 58% at 140°C. β-pinene oxide produced more aldehydes at 80°C, than that at 110 and 140°C. The percentage yield of aldehydes over various catalysts ranged from 41 to 59 at 80°C for β-pinene oxide, and at 140°C the yield varied from 10 to 13%. Al_2O_3-Eu_2O_3, and Al_2O_3-Nd_2O_3 are found to be best catalysts for α-pinene oxide isomerization at 80, 110, and 140°C , while Al_2O_3-Y_2O_3 showed 85% conversion to products at 140°C for β-pinene oxide isomerization.

3.5 Transformations of Limonene Oxides

Earlier Studies

Humbert and Guth performed the first isomerization of d-limonene oxide in a heterogenous catalyst system[82] over Al_2O_3 at 200°C. The main products being carveols, dihydrocarvone, methyl-1-isopropenyl-3-cyclopentyl methanol. When Nigam and Levi chromatographed limonene oxide over active alumina it isomerized mainly to allylic alcohols, exo-and endo-carveols along with dihydrocarvone, perillyl alcohol and 8(9)-p-menthene 1,2-diol. The product distribution varied with nature of alumina used[83]. Settine and co-workers in 1964 observed the rearrangement of limonene oxide over solid zinc bromide in refluxing benzene to aldehyde and ketone[97].

(35) , carvone (36), cis and trans dihydro carvone (6) cis and trans-exo-carveol (4) and cis and trans-endo-carveol (5).



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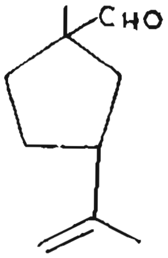

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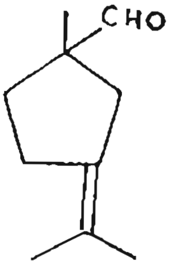

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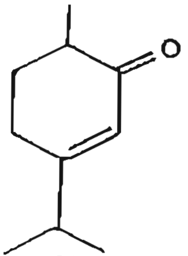

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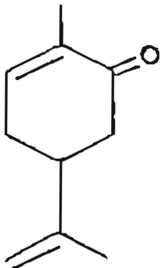

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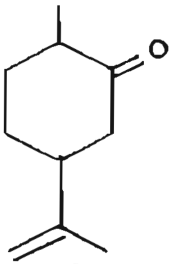

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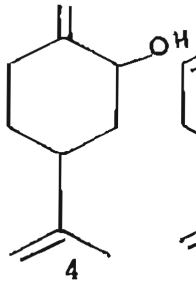

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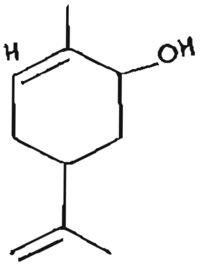

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In these reactions studied, the selectivity for the formation of various products depended on the catalyst used. Acidic catalysts like H_2SO_4/SiO_2, SiO_2-Al_2O_3, BF_3-etherate and $LiClO_4$ gave mainly carbonyl compounds. Among the catalysts Bronsted acids facilitate double bond migration reactions. Bifunctional catalysts like TiO_2-ZrO_2, TiO_2 etc. formed allylic alcohols. Among allylic alcohols electronic factors play a role in the exo-and endo-alcohol formation. Basic oxides like CaO, BaO, MgO are inactive to the isomerization of limonene oxide while metallic sulphates like $NiSO_4$ and $FeSO_4$ produced different products depending on their calcination temperature.

There are reports in literature for the use of Y_2O_3, La_2O_3 and Ce_2O_3 in the isomerization of 3-carene. No other catalysts were used in the isomerization reactions of terpenes. A number of perfumery compounds like carvone were reported to be formed from limonene oxide. Hence in the present study a number of alumina-rare earth oxide catalysts like Al_2O_3-Y_2O_3, Al_2O_3-Sm_2O_3, Al_2O_3-Pr_6O_{11}, Al_2O_3-Nd_2O_3 and Al_2O_3-Eu_2O_3 were used.

3.5.1 Transformations of (+) - Limone Oxide [1-Methyl-4-(1-methyl ethenyl)-7-oxabicyclo[4.1.0] heptane-R] (3)

Materials

(+)-Limonene oxide was 97% pure and is a 1:1 mixture of *cis and* trans epoxide supplied by Aldrich Chemical Company. Solvents, toluene and *xylene were analytical grade* reagents which were purified as in section 3.3.2

3.5.2 Experimental

Reactions at 110°C

(+)-Limonene oxide (100 mg, 0.65 m mol), 500 mg of catalyst and 5 ml solvent (toluene) were stirred at 110°C. Reaction rate was monitored by TLC. After 20 hours reaction was found to be slow. Reaction mixture was filtered to remove the catalyst. Catalyst refluxed with methylene chloride and filtered. All filtrates were combined together and sovlent removed. Reaction was repeated for all five binary oxide catalysts.

Reactions at 140°C

The same procedure at 110°C was repeated for all five binary oxide catalysts at 140°C. The reaction was monitored after 1 hr by GLC analysis and percentage conversion ranged from 32 to 50%. Al_2O_3-Eu_2O_3 and Al_2O_3-Pr_6O_{11} showed maximum conversion of 50%. The reactions at 140°C were monitored by TLC and it was found that after 8 hr, the reactions were found to be slow. The catalyst was separated from reaction mixture and extracted with methylene chloride. All filtrates combined together and solvent removed.

3.5.3 Preparation of Authentic Samples

3.5.3.1 Preparation of **Methyl** (3-Iso **propenyl** cyclopentyl) ketone (72)

Materials

(+)-Limonene oxide, $ZnBr_2$ (both supplied by Aldrich Chemical Company). Solvent benzene was supplied by BDH is a guaranteed reagent and dried by distilling over sodium metal.

Experimental

Methyl (3-iso propenyl cyclopentyl) ketone was prepared by following the procedure of R.L. Settine and co-workers[97].

39g (0.26 mol) of limonene oxide was added to refluxing benzene. To that solution 1 g of freshly fused zinc bromide added. During addition of $ZnBr_2$ external heatiang was discontinued. The mixture was refluxed for 2 hours and 200 ml water added. The benzene solution was washed with water to remove zinc salts. The solution was extracted and solvent removed. The crude material was distilled in vacuum and the second fraction obtained at 75°C (10 mm of Hg) was collected. In GLC analysis this fraction contained two components which were identified as methyl (3-isopropenyl cyclopentyl) ketone and dihydro carvone. IR and NMR of the mixed ketones were taken. Yield 23 g (57%). Purity of methyl-3 isopropenyl cyclopentyl ketone was 53% by GLC analysis.

3.5.3.2 Preparation of carveols(4',4, 56,5)

Materials

(+)-Limonene oxide, Aluminium Isopropoxide supplied by E. Merck (India) Ltd.

Experimental

16g of (+)-limonene oxide (0.12 mol) and 1 g of aluminium isopropoxide were heated under coarse vacuum at 150 mm of Hg. After a vigorous reaction, temperature of the reaction mixture rose upto 160°C, and reaction was allowed to continue for 10 minutes and the distillate obtained was collected. The material obtaind was a mixture of four isomeric allylic alcohols which separated on GLC (Column used ov 17 (10%) I.D 3.1 mm, 1.8 m length, order of elution being trans-exo-alcohol cis-exo-alcohol, trans-endo and cis-endo alcohol).

3.5.1.3 Preparation of Limonene Diol (8)

Materials

(+)-Limonene oxide, supplied by Aldrich Chemical Company. Tetrahydrofuran guaranteed reagent supplied by E.Merck (India) Ltd, 1% H_2SO_4 solution. Ethyl acetate and hexane are guaranteed reagents supplied by BDH, which was further purified by distillation over dry sieves. Silica gel used for column chromatography was 60-120 mesh supplied by [illegible] (India) Ltd.

Experimental

Diol was prepared by the method of Arbuzov[158]. 1.4 g of (+)-limonene oxide was taken in 20 ml tetrahydrofuran and 11 ml water. It was cooled to 0°C and 2.5 ml of 1% H_2SO_4 added and kept at 0°C for 30 minutes. After that period, reaction mixture attained room temperature, it was stirred for 2 hr. Then 50 ml of water added and extracted with methylene chloride. Extract was washed with aqueous $NaHCO_3$ solution and dried over anhydrous sodium sulphite. Solvent removed and the diol mixture was purified by column chromatography.

A chromatographic column was filled with a slurry of silica gel in hexane-ethyl acetate (9:1) mixture. Column was eluted with hexane-ethyl acetate (9:1) and first diol collected. Yield 1.11 g. Purity of the diol was found to be 86% by GLC analysis. Second diol was collected by eluting the column with hexane-ethyl acetate (7:3) mixture. Yield obtained was 0.13 g. Purity of the diol was found to be 85% by GLC analysis.

3.5.4 Identification of Products

The reaction mixture was analysed by GLC and GC-MS. Constituents were identified by comparison of their relative retention time with authentic samples. Linalyl acetate was used as the internal standard. The MS data given in the text are in the decreasing order of abundance.

Compound 4' was identified as trans-exo-carveol by its RRT and MS.

41(100), 55, 67, 79, 91, 109, 119, 134, 105, 123.

Compound 4 was identified as cis-exo-carveol by its RRT and MS.

41(100), 81, 67, 55, 107, 93, 121, 136, 152.

Compound 72 was identified as methyl (3-isopropenyl cyclopentyl) ketone by comparing its RRT with authentic sample and MS.

41(100), 55, 109, 84, 91, 69, 77, 119, 105, 134, 123, 152.

Compound 56 was idenified as trans-endo-carveol by its RRT and MS.

119(100), 134, 91, 92, 93, 109, 84.

Compound 5 was identified as cis-endo-carveol by its RRT and MS.

84(100), 134, 109, 41, 55, 119, 83, 91.

Compound 36 was identified as carvone by comparing RRT with an authentic sample supplied by Fluka (A.G) Chem. U.S.A. and MS.

82 (100), 54, 41, 93, 108, 79, 58, 67.

Compound 8 was identified as limonene diol by comparing its RRT with authentic sample and MS.

43(100), 71, 67, 55, 82, 108, 88, 137, 152, 119, 101.

3.5.5 Results and Discussion

At 110°C over all binary oxide catalysts conversion ranged from 65 to 76%. Minimum conversion 65% was observed over Al_2O_3-Y_2O_3 and Al_2O_3-Pr_6O_{11} produced maximum conversion of 76%. At 110°C Al_2O_3-Eu_2O_3 produced 75% conversion to products. Compared to other catalysts Al_2O_3-Eu_2O_3 and Al_2O_3-Pr_6O_{11} were found to be better catalysts than others.

At 140°C, when reaction mixture was analysed by GLC, conversion ranged between 32 to 50%. Maximum conversion 50%

Table 23

Reaction at 110°C for 20 hr

Catalyst	Conversion %	Product % 4'	4	72	56	5	36	8
Al_2O_3-Y_2O_3	65	12	10	9	9	15	9	30
Al_2O_3-Eu_2O_3	75	35	20	-	13	-	20	14
Al_2O_3-Pr_6O_{11}	76	33	-	20	12	-	20	10
Al_2O_3-Sm_2O_3	70	22	-	-	21	10	14	25
Al_2O_3-Nd_2O_3	72	30	15	-	15	-	15	20

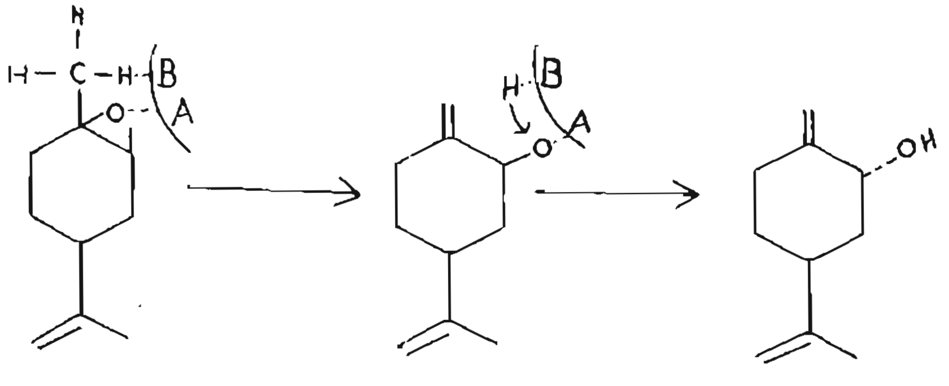
Table 24

Reaction at 140°C for 1 hr

Catalyst	Conversion %	Product % 4'	4	72	56	5	36	8
Al_2O_3-Y_2O_3	32	18	6	24	-	-	-	42
Al_2O_3-Eu_2O_3	50	36	8	28	-	-	16	10
Al_2O_3-Pr_6O_{11}	50	29	-	14	17	-	14	8
Al_2O_3-Sm_2O_3	40	27	10	24	-	-	18	9
Al_2O_3-Nd_2O_3	38	30	10	-	5	-	15	12

After 8 hr at 140°C the yield of trans-exo-carveol reached 37% in the case of Al_2O_3-Y_2O_3. Except Al_2O_3-Y_2O_3 and Al_2O_3-Pr_6O_{11}, other catalysts showed a decrease in the production of exo-carveol. Among the five binary oxide catalysts Al_2O_3-Y_2O_3 showed a steady increase in the percentage production from 12 to 37 with rise in temperature from 110°C to 140°C.

The formation of allyl alcohol can be illustrated as follows. The epoxide gets adsorbed on the catalyst surface through oxygen atom on an acidic site. The epoxide ring opens up giving a tertiary carbonium ion. A proton from methyl group is abstracted by a basic site resulting in an exocyclic double bond. The proton attached to the basic site by weak forces may shift to the oxygen atom.



A : Acidic site B : Basic site

For reaction at 110°C , there exists a correlation between the production of trans-exoc-arveol with acid amounts at

Ho $\leq$ +6.8 and Ho $\leq$ +1.5. As the acid amount increased the yield of carveol also increased, which is illustrated in Fig.21. From reaction mechanism it is clear that allyl alcohol formation requires the coexistence of acidic and basic sites on catalyst surface. With the increase in basicity at pKBH +15, an increase in yield of trans-exo-carveol was observed.

3.5.5.2 Cis-exo-carveol [2-Methylene cyclohexane 1-ol-5 (1-methyl ethenyl) cis] (4)

Binary oxides like Al_2O_3-Y_2O_3, Al_2O_3-Eu_2O_3 and Al_2O_5-Nd_2O_3 formed cis-exo-carveol at 110°C. At 140°C when reaction was monitored after 1 hr, the yield of alcohol varied from 6 to 10%. At 140°C after 8 hr , the yield of exo-carveol increased and ranged from 22 to 30%. No cis-exo-carveol was formed over Al_2O_3-Pr_6O_{11} at 110°C but it yielded maximum (30%) at 140°C.

3.5.5.3 Trans-endo-carveol [2-Cyclohexane-1-ol,2-methyl -5(1-methyl ethenyl) - trans] (56)

Over various binary oxide catalysts the yield of trans-endo-carveol varied from 9 to 21% at 110°C. Al_2O_3-Sm_2O_3 produced maximum yield 21% while Al_2O_3-Nd_2O_3 yielded only 15%. Least amount of trans-endo-carveol (9%) was formed over Al_2O_3-Y_2O_3. At 140°C when reaction mixture was analysed after 1 hr, Al_2O_3-Pr_6O_{11} and Al_2O_3-Nd_2O_3

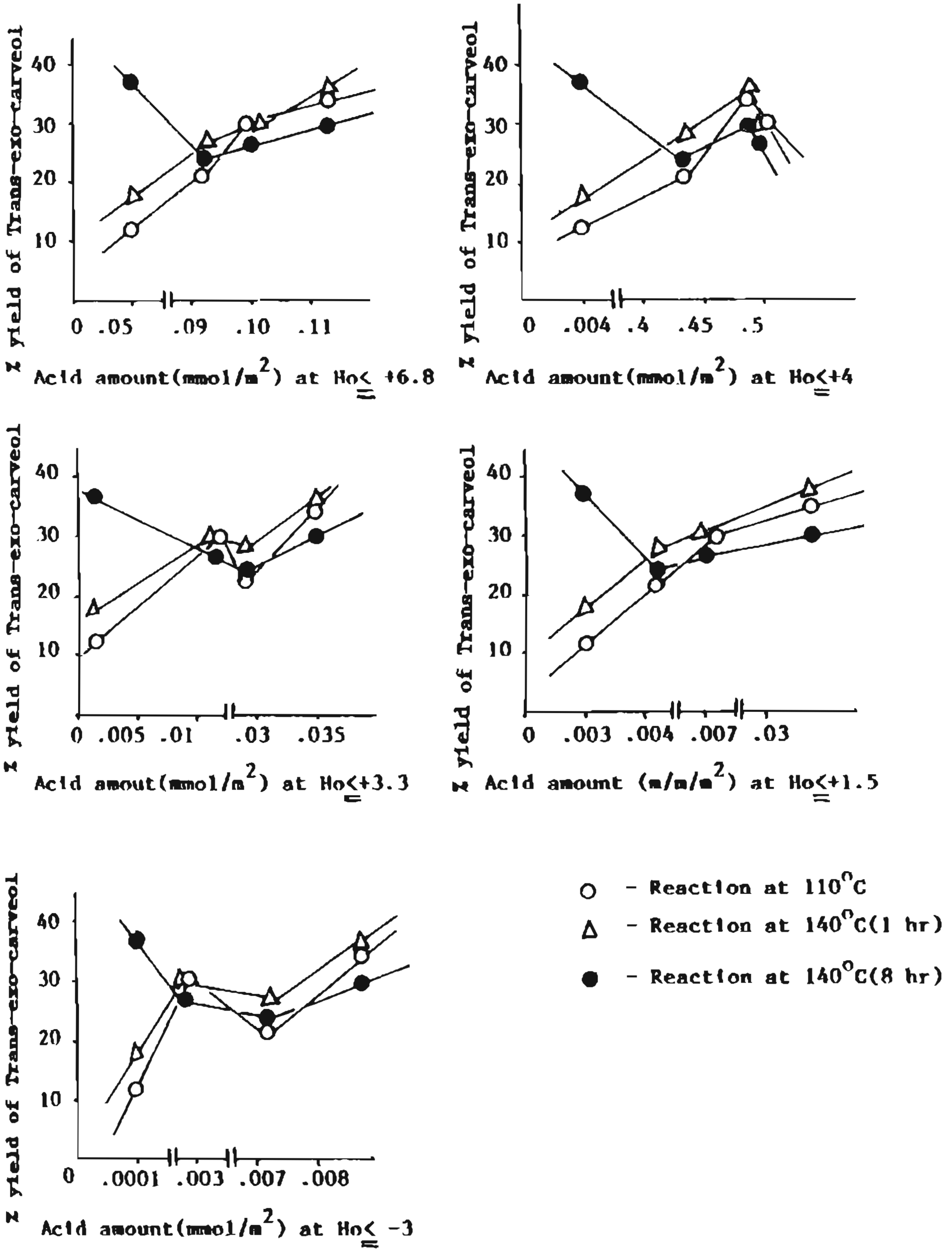
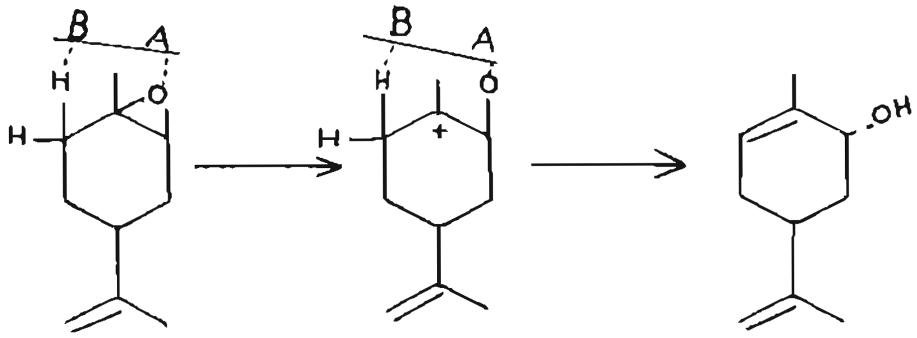


Fig. 21 Variation in the percentage production of Trans-exo-carveol with acid amount.

produced trans-endo- carveols. After 8 hr at 140°C the yield of alcohol changed from 13 to 23% over Al_2O_3-Eu_2O_3. When temperature increased from 110 to 140°C the percentage yield of trans-endo carveols decreased over Al_2O_3-Y_2O_3, Al_2O_3-Sm_2O_3 and Al_2O_3-Nd_2O_3.

The formation of trans-endo-carveol can be illustrated as given below. The epoxide ring opens up when the oxygen gets loosly bonded to an acid site, and a tertiary carbonium ion is formed. A basic site adjacent to the acidic site abstracts a proton from ring carbon and leaves a double bond inside the ring. The proton migrates to the oxygen from basic site which then leaves the catalyst surface to form the alcohol.



A: Acidic site B: Basic site

As evident from Fig.22 the yield of trans-endo-carveol increased with acid amount in m mol/m^2 at Ho $\leq$ -3. For basicity values at H_15 a similar trend can be

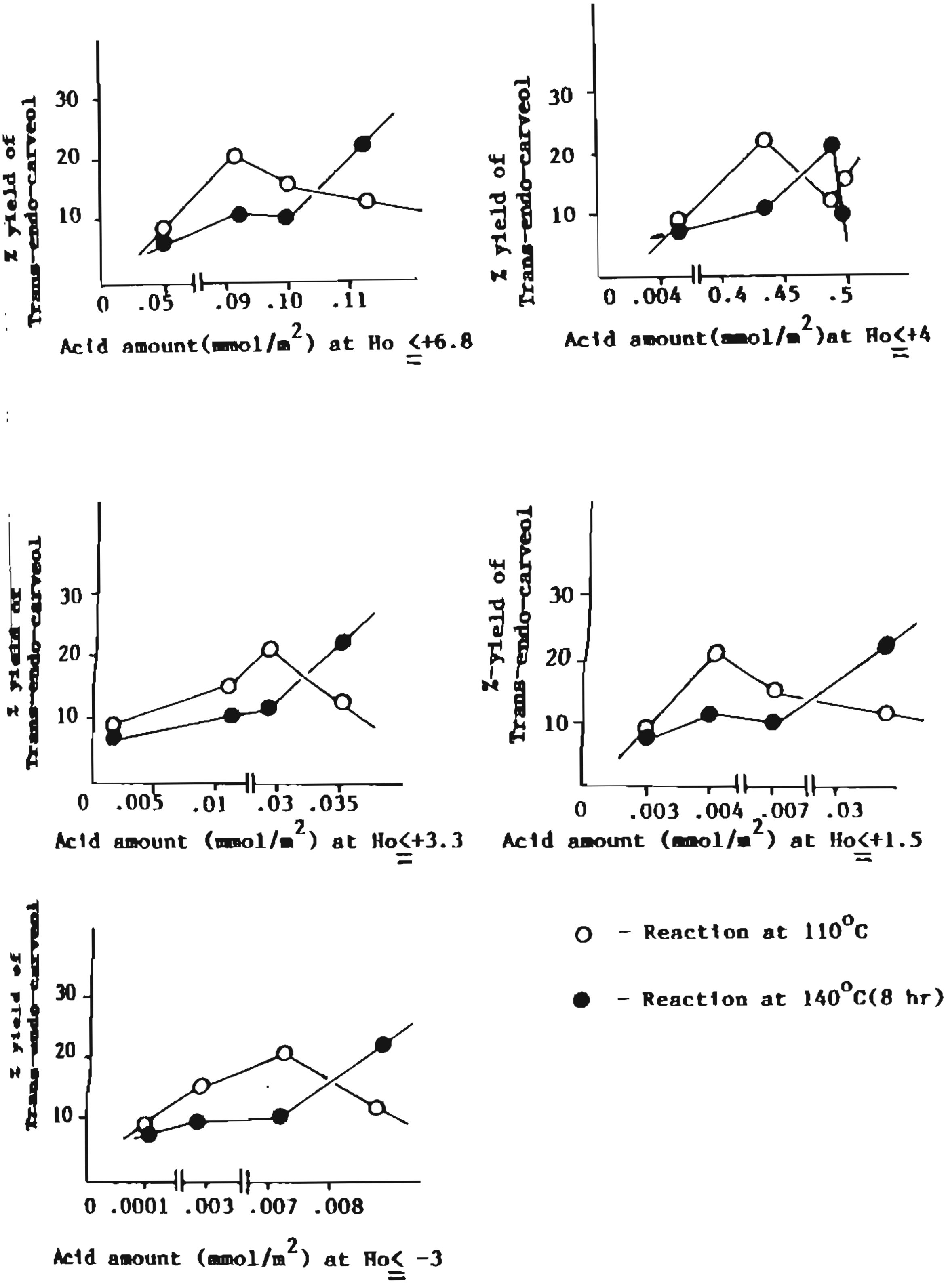


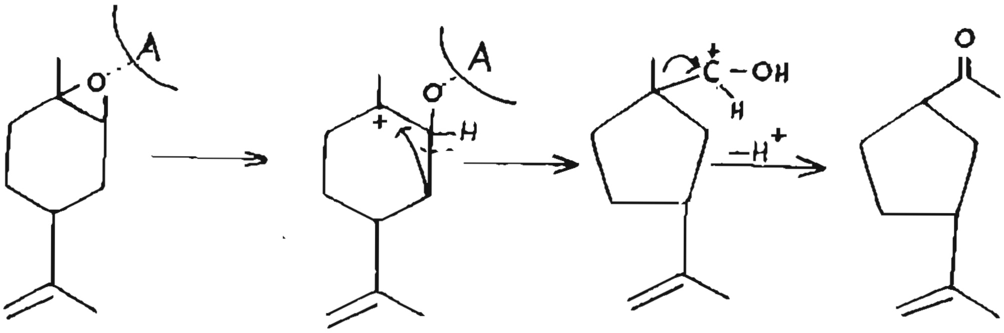
Fig.22 Variation in the percentage production of Trans-endo-carveol with acid amount.

observed. Over other acid amounts the variation in the yield of trans-endo-carveol is not regular.

3.5.5.4 Methyl-3-isopropenyl cyclopentyl ketone (72)

Al_2O_3-Y_2O_3 and Al_2O_3-Pr_6O_{11} produced cyclopentyl ketones at 110°C. When reaction was conducted at 140°C and after 1 hr all catalysts except Al_2O_3-Nd_2O_3 produced ring contracted ketone and yield varied from 14 to 28%. Al_2O_3-Eu_2O_3 produced maximum yield of 28% and 24% yield was observed over Al_2O_3-Y_2O_3 and Al_2O_3-Sm_2O_3. When reaction mixture was analysed after 8 hr at 140°C no ketone formation was observed.

The formation of ketone can be represented as below. The epoxide gets adsorbed on catalyst surface through oxygen atom and epoxide ring opens up. A tertiary carbonium ion is produced followed by a ring contraction. A methyl group migrates to the carbonium ion which is followed by a proton elimination to give the ketone.



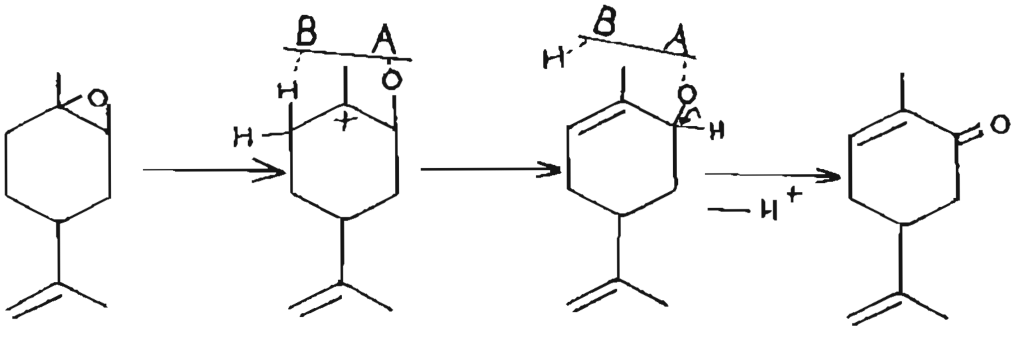
A : Acid site

There is no regular variation in the percentage production of ketone with acid amount at various acid ranges. At 140°C, the ketone formed may get transformed to exo-carveol because no ketone formation was obsrved at that temperature and there is a clear increase in the amount of cis-exo-carveol.

3.5.5.5 Carvone [2-Cyclohexene-1-one, 2 methyl-5-[1-methyl ethenyl]] (36)

The yield of carvone ranged from 9 to 20% over various catalysts at 110°C. Al_2O_3-Eu_2O_3 and Al_2O_3-Pr_6O_{11} produced maximum yield of 20%. As temperature increased to 140°C, the percentage yield decreased. At 140°C, when reaction mixture was analysed after 1 hr, Al_2O_3-Eu_2O_3 produced 16% and Al_2O_3-Pr_6O_{11} produced 14% of carvone. When reaction mixture was analysed after 8 hr at 140°C the yield decreased to 15% over Al_2O_3-Eu_2O_3 and 11% over Al_2O_3-Pr_6O_{11}. At 140°C over various catalysts the yield varied from 4 to 15%.

The mechanism for the formation of carvone is illustrated as follows. The epoxide gets adsorbed on an acidic site through oxygen atom and a proton from ring carbon is extracted by a basic site on catalyst surface. The epoxide ring opens up and a tertiary carbonium ion is formed which eliminates a proton and an unsaturation is formed on the ring. Finally the ketone gets desorbed from the catalyst surface.



A : Acidic site B : Basic site

As evident from Fig.23 there exists some correlation for the formation of carvone with acid amount at 110^{o}C and 140^{o}C (8 hr) for Ho $\leq$ +6.8 and Ho $\leq$ +1.5. As the acid amount increased, the percentage production of carvone also increased. There exists no correlation for yield of carvone with acid amount at other acid strengths.

3.5.5.6 8,(9)-p-menthene-1,2-diol (8)

All binary oxide catalysts produced diol in 10 to 30% yield at 110^{o}C. Highest yield 30% was observed over Al_2O_3-Y_2O_3 and 25% yield was obtained over Al_2O_3-Sm_2O_3. At 140^{o}C when analysis was carried out after 1 hr, the percentage of diol decreased with the exception of Al_2O_3-Y_2O_3. Al_2O_3-Y_2O_3 produced 42% diol. At 140^{o}C after 8 hr of reaction, Al_2O_3-Y_2O_3 produced 24% diol and Al_2O_3-Sm_2O_3 produced 30% while Al_2O_3-Nd_2O_3 yielded 21% diol.

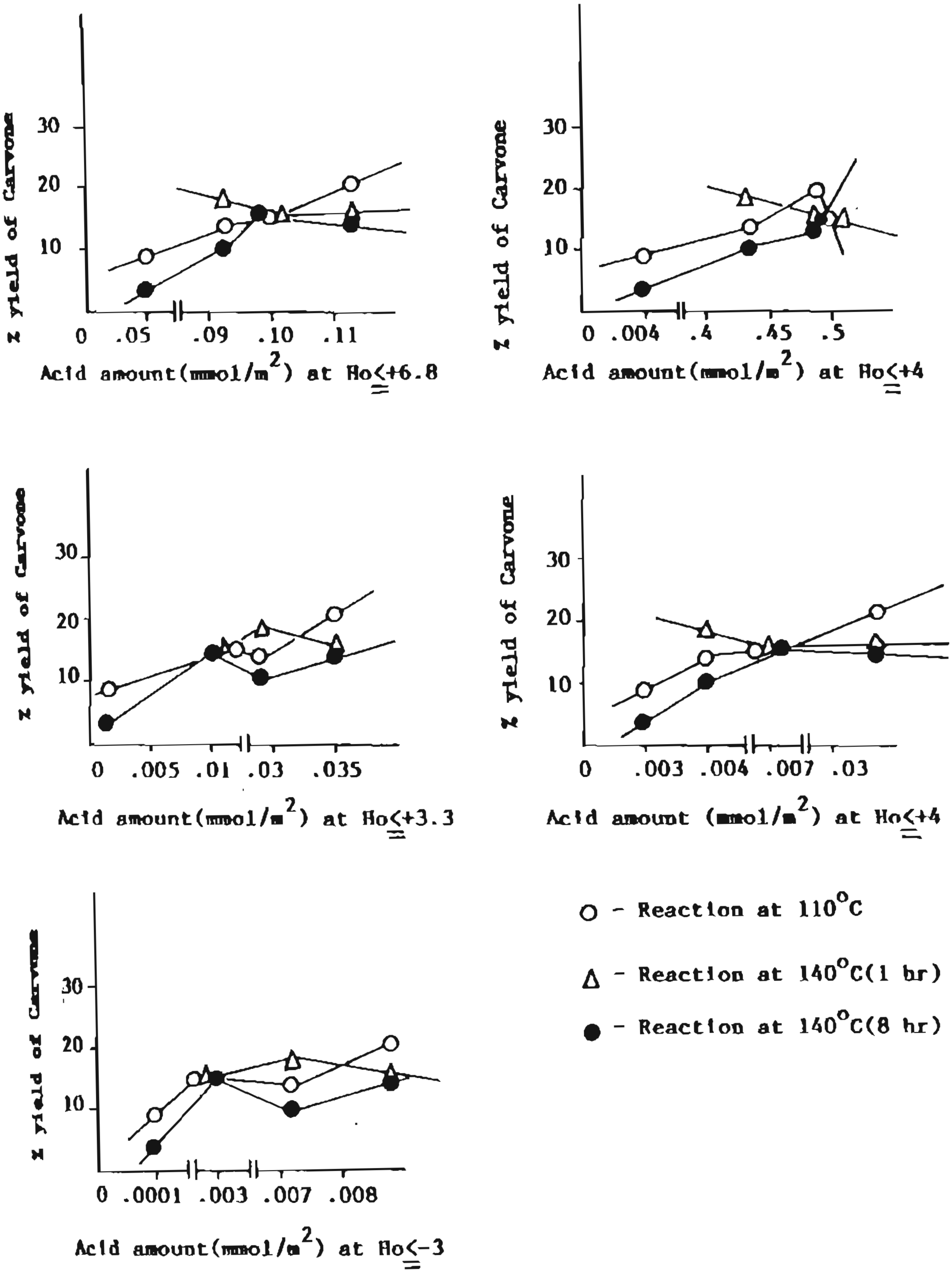
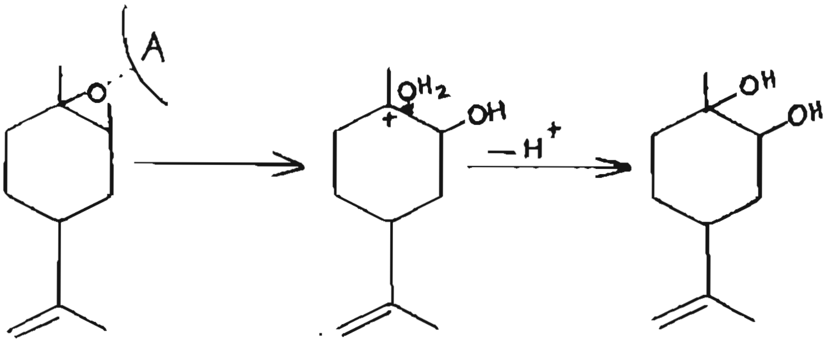


Fig. 23. Variation in the yield of Carvone with acid amount

When reaction temperature changed from 110 to 140°C the yield of diol decreased from 30 to 24 in the case of Al_2O_3-Y_2O_3 and Al_2O_3-Pr_6O_{11} showed an increase from 10 to 20%. Al_2O_3-Eu_2O_3 showed a decrease in the percentage yield of diol from 10 to 8 when temperature changed from 110 to 140°C.

The formation of diol can be illustrated as follows. The epoxide oxygen attaches itself to the catalyst's surface. The initial adsorption could be due weak Vander waals forces. The substrate gets adsorbed on an acid site on the catalyst surface through oxygen atom. Epoxide ring opens up and a tertiary carbonium ion is formed, which is attacked by H_2O by its lone pair of electrons on oxygen which results in the formation of a diol with the elimination of a proton.



A: Acid site

There exists no direct correlation with percentage yield of diol and acid strength. An inverse relationship is observed for the yield of diol at 110°C with acid amount at Ho $\leqq$ +6.8. As the acid amount increased the percentage yield of diol decreased.

Cis-endo-carveol (5) is a minor product formed in 15% and 10% only over Al_2O_3-Y_2O_3 and Al_2O_3-Sm_2O_3 at 110°C. At 140°C no catalysts produced cis-endo-carveol.

For the two reactions carried out at 110°C and 140°C allyl alcohols were the major products formed over all catalysts. Al_2O_3-Eu_2O_3 was found to be the best catalyst among others. The purpose in carrying out the isomerization was to obtain carvone, the high value perfumery product which could be obtained only in yields varying from 5-20%. Allyl alcohols the major product produced could be converted to carvone by oxidation.

3.5.6 Effect of Catalysis Reaction on the Chiral Carbon at C_4 in the Transformation of (+)-Limonene Oxide

In (+)-limonene oxide, the chiral carbon at C_4 has the R-configuration. In order to find out whether any change is happening at C_4, one of the products, namely carvone was isolated by elaborate column chromatography from the reaction products, on the reaction of (+)-limonene oxide with Al_2O_3-Pr_6O_{11}. The carvone isolated had an $[\alpha]_D$-65°. The reported value for R(-) carvone is $[\alpha]_D^{20}$ - 61°. It is very clear from this that no configurational change has *taken place at the C_4 chiral carbon.*

3.6 Transformation of (-)-Limonene oxide [1-methyl-4-(1-methyl ethenyl)-7-oxabicyclo [4.1.0] heptane-s] (73)

3.6.1 Earlier studies

d-Limonene oxide was used by a number of investigators in heterogeneous reactions. So far no reports appear in literature on the isomerization studies of (-)-limonene oxide over any binary oxide catalysts.

3.6.2 Preparation of m-chloro perbenzoic Acid

m-chloro perbenzoic acid was prepared by the standard procedure given by Mc Donald[159].

3.6.3 Preparation of (-)-Limonene oxide

Materials

(-)-Limonene (97% pure supplied by Aldrich Chemical Company), m-chloroperbenzoic acid, ether, $NaHCO_3$ solution and anhydrous sodium sulphate.

Experimental

(-)-Limonene oxide was prepared by the procedure given by E.E. Royals and Harrell[96]. (-) Limonene, 30 g (0.2205 mol) *added in one lot to m-chloroperbenzoic acid* solution (200 ml) in an ice bath. The reaction mixture was kept in an ice bath for 2 hr and transferred to a refrigerator. The reaction rate was monitored by TLC. After 24 hr, reaction mixture was filtered to remove free acid. The filtrate was washed with aqueous $NaHCO_3$ solution to remove acid. Finally the mixture was dried over anhydrous sodium sulphate and solvent removed. The crude reaction mixture was distilled under reduced pressure and the second fraction was collected at 70-72°C (10 mm Hg). Yield 18 g (60%) and the product obtained was 82% pure by GLC analysis. This fraction again fractionally distilled and second fraction collected at 70°C (10 mm Hg) yielded 10 g. The product obtained was 94% pure by GLC analysis and it is assumed to be a 1:1 mixture of cis and trans epoxide.

3.6.4 Reactions of (-)-Limonene oxide

Reactions at 110°C

(-)-Limonene oxide 200 mg (1·3 m mol), 1 g catalyst and 10 ml solvent (toluene) were stirred under reflux. Reaction rate was monitored by TLC at every 30 minutes interval. After 10 hr reaction was found to be very slow. Reaction mixture was filtered and catalyst extracted with methylene chloride. All extracts combined together and solvent removed. The same procedure was repeatead for all five binary oxide catalysts.

Reactions at 140°C

Reactions at 140°C were done using xylene as a solvent. Reaction time was 8 hr and same procedure was repeated for all catalysts. Reaction procedure was same as that at 110°C.

3.6.5 Preparation of Authentic Samples

3.6.5.1 Preparation of Carveols (74, 74',75, 76)

Materials

(-) Limone oxide, aluminium isopropoxide (supplied by Aldrich Chemical Company)

Experimental

Carveols were prepared by the method of Eschinasi[99]. Reaction procedure was same as given in section 3.5.3.2. Yield obtained 73%. Purity of the carveols were checked by GLC analysis in an ov 17 (10%) column at temperature programme (80-200°C). Order of elution for carveols was trans-exo-carveol, cis-exo-carveol, trans-endo-carveol and cis-endo-carveol. Purity of the four diols were checked by GLC analysis.

3.6.5.2 Preparation of Limonene Diol(78)

Diol was prepared by the method given by Arbuzov[158].

Materials

(-)-Limonene oxide, THF supplied by E. Merck (India) Ltd, and 1% H_2SO_4 solution.

Experimental

Reaction procedure same as in section 3.5.3.3. Diols purified by column chromatography. Purity of the products were found to be 83 and 90% by GLC analysis.

3.6.6 Identification of Products

The reaction mixture was analysed by GLC and constituents were identified by comparison of their relative retention time with authentic samples. P-cymene was used as the internal standard in GLC analysis.

Compound 74 was identified as trans-exo-carveol by its RRT.
Compund 75 was identified as cis-endo-carveol by its RRT.
Compound 76 was identified as trans-endo-carveol by its RRT.
Compound 77 was identified as carvone by comparing its relative retention time with authentic sample.

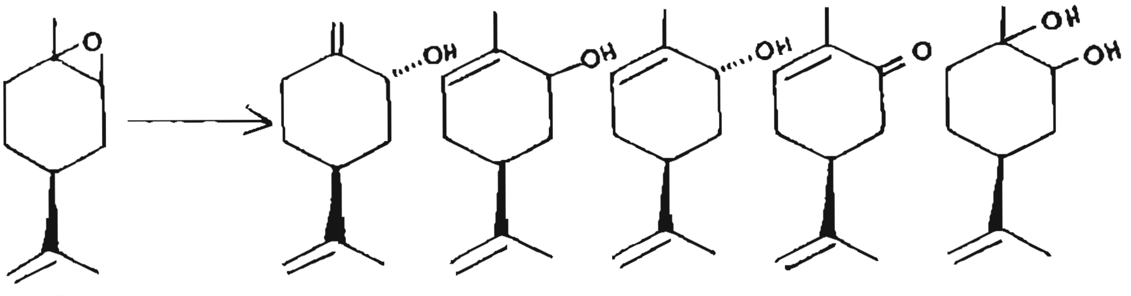
Compound 78 was confirmed as limonene diol by comparing its RRT with an authentic sample prepared.

3.6.7 Results and Discussion

When isomerization was carried out at 110^{o}C, the various binary oxide catalysts yielded 27 to 66% products. Al_2O_3-Nd_2O_3 produced maximum conversion of 66%. Al_2O_3-Sm_2O_3 and Al_2O_3-Eu_2O_3 yielded 63% and 62% products respectively. Least percentage conversion was observed over Al_2O_3-Y_2O_3.

The percentage conversion varied from 40 to 81 over various catalysts at 140°C. Al_2O_3-Nd_2O_3 produced maximum conversion of 81% and Al_2O_3-Eu_2O_3, Al_2O_3-Sm_2O_3 produced 80% conversion. At 140°C also least conversion was observed over Al_2O_3-Y_2O_3. Among the five binary alumina-rare earth oxides, Al_2O_3-Nd_2O_3 was found to be best catalyst for the isomerization of (-) limonene oxide at both temperatures of 110 and 140°C.

(-)-Limonene oxide rearranges over binary oxide catalysts to give trans-exo-carveol (74), cis-endo-carveol (75), trans-endo-carveol (76), carvone (77) and limonene diol (78).



73 74 75 76 77 78

The activity and selectivity of various catalysts are given in Tables 26 and 27.

Table 26

Activity of Catalysts at 110°C for (-)-Limonene Oxide Reaction (1 hr)

Catalysts	Conversion %	Product % 74	75	76	77	78
Al_2O_3-Y_2O_3	27	33	35	17	7	8
Al_2O_3-Sm_2O_3	63	20	24	4	3	46
Al_2O_3-Eu_2O_3	62	25	32	7	4	32
Al_2O_3-Nd_2O_3	66	26	28	8	8	15
Al_2O_3-Pr_6O_{11}	35	43	24	33	4	30

Table 27

Activity of Catalysts at 140°C for (-)-Limonene Oxide Reaction (8 hr)

Catalysts	Conversion %	Product % 74	75	76	77	78
Al_2O_3-Y_2O_3	40	27	25	-	11	18
Al_2O_3-Sm_2O_3	80	40	16	6	22	16
Al_2O_3-Eu_2O_3	80	27	26	13	12	15
Al_2O_3-Pr_6O_{11}	70	30	30	14	16	8
Al_2O_3-Nd_2O_3	81	30	25	10	14	21

3.6.7.1 Trans-exo-carveol [2-Methylene cyclohexane-1-01-5 *(1-methyl ethenyl) trans] (74)*

At 110°C *all binary oxides yield trans-exo-carveol* and the percentage yield varied from 20 to 43. Maximum yield of 43% was observed over Al_2O_3-Pr_6O_{11} and minimum (20%) was observed over Al_2O_3-Sm_2O_3. Al_2O_3-Y_2O_3 produced 33% while Al_2O_3-Eu_2O_3 produced 25% yield.

When reaction was carried out at 140°C the variation in the percentage production of trans-exo-carveol was irregular. Al_2O_3-Y_2O_3 and Al_2O_3-Pr_6O_{11} showed a decrease in the production while other catalysts showed an increase in the yield of products. Maximum yield 40% was observed over Al_2O_3-Sm_2O_3, Al_2O_3-Pr_6O_{11} and Al_2O_3-Nd_2O_3 produced 30% yield of trans-exo-carveol. The mechanism for the formation of trans-exo-carveol is explained in section 3.5.5.1

As evident from Fig. 24 at various acid strengths with increase in acid amounts, the percentage yield of alcohol increase first then decreases and again show a small increase. An increase in the percentage production of allyl alcohol with basic amount at Ho+15 was observed.

3.6.7.2 Cis-endo-carveol [2-Cyclohexane-1-01,2-methyl-5 (1-methyl ethenyl) - cis] (75)

Over various catalysts, the yield of endo-carveol varied from 24 to 35% at 110°C. Maximum yield 35% was observed over Al_2O_3-Y_2O_3 and Al_2O_3-Eu_2O_3 produced 32% yield

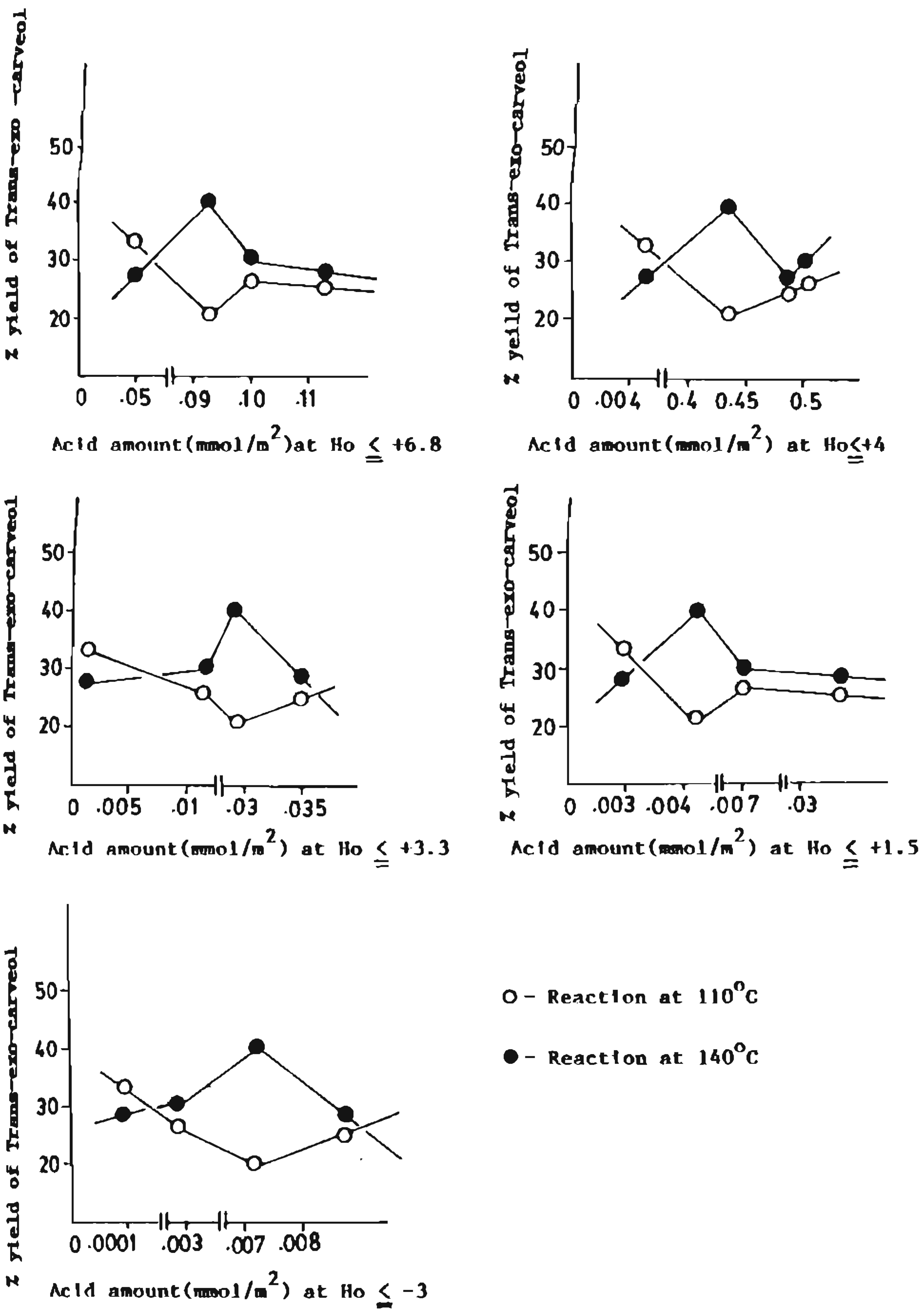
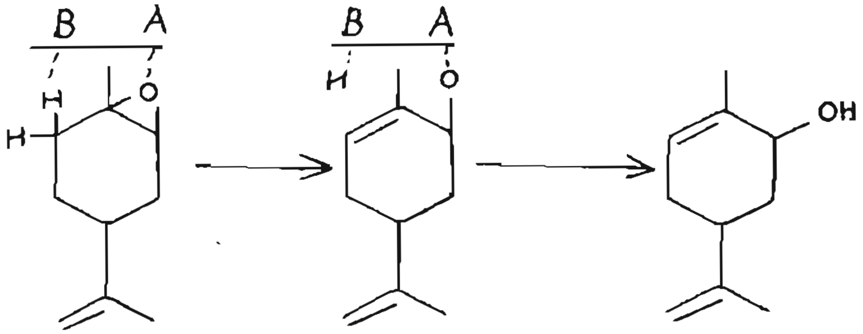


Fig.24 Variation in the percentage yield of Trans-exo-carveol with acid amount.

of cis-endo-carveol. Al_2O_3-Sm_2O_3 and Al_2O_3-Pr_6O_{11} produced *lowest yield, 24%.*

The percentage yield varied from 16 to 30% at 140°C. Al_2O_3-Pr_6O_{11} produced maximum yield of cis-endo-carveol (30%) and increase in yield of carveol was observed only over Al_2O_3-Pr_6O_{11}. All other catalysts showed a decrease in the yield of cis-endo-carveol, with rise in temperature from 110 to 140°C. Al_2O_3-Sm_2O_3 produced a minimum yield of 16%.

The formation of endo-carveol from epoxide can be depicted as follows. The expoxide oxygen gets itself attached to an acidic site and epoxide ring opens to a tertiary carbonium ion. A proton from ring carbon is abstracted by a base to give an unsaturation in the ring and the proton is transferred from basic site to oxygen atom and an alcohol is formed.



A : **Acidic site** B: **Basic site**

In Fig. 25 acid strength at various Ho valaues are plotted against percentage yield of cis-endo-carveol. There is no regular variation in the yield of alcohol with acid

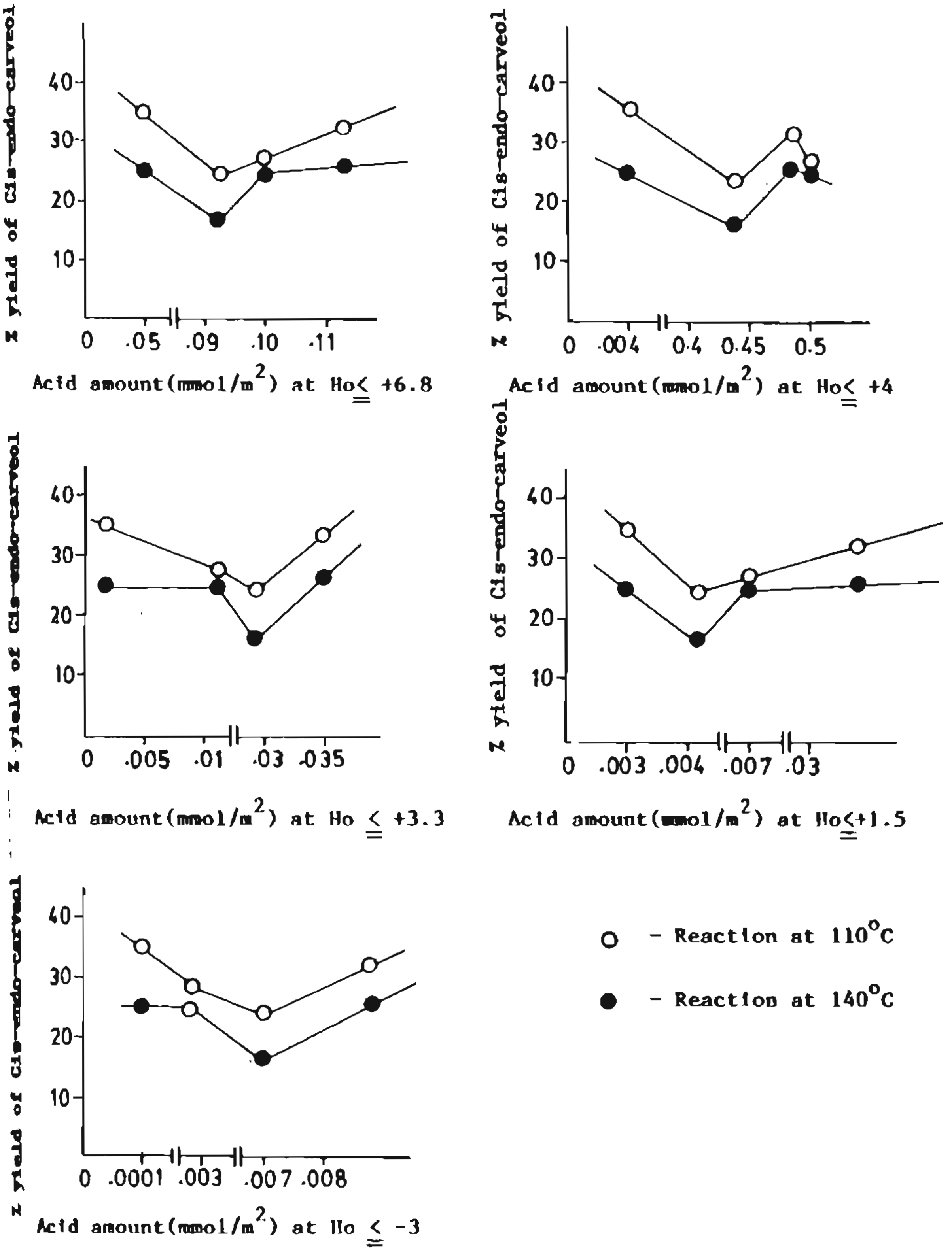


Fig. 25. Variation in the percentage yield of Cis-endo-carveol with acid amount

strength. So no direct correlation can be obtained from the figure. An increase in the yield of cis-endo-carveol was observed for basicity values at pKBH +15.

3.6.7.3 Trans-endo-carveol [2-Cyclohexane-1-01 2-methyl-5 (1-methyl ethenyl) - trans] (76)

At 110°C Al_2O_3-Y_2O_3 produced 17% of trans-endo carveol and Al_2O_3-Pr_6O_{11} produced 33% alcohol. All other catalysts produced only 4 to 8% yield. At 140°C the percentage yield varied from 6 to 14. Al_2O_3-Pr_6O_{11} produced maximum yield of 14 and Al_2O_3-Eu_2O_3 produced only 13% yield of trans-endo-carveol.

A close examination of the Fig. 26 shows that there exists a correlation of acid amount with percentage yield of alcohol at Ho $\leqq$ +6.8 and +1.5 for reaction at 140°C. At other acid strengths no direct relationship was observed. So no correlation was possible at other cases.

3.6.7.4 Carvone [2 cyclohexane-1-one, 2-methyl-5-(1-methyl ethenyl)] (77)

The yield of carvone is small varying from 3 to 8% over various catalysts at 110°C. Al_2O_3-Nd_2O_3 produced maximum yield of carvone (8%). Over all catalysts as tmperature changed to 140°C the yield increased. Al_2O_3-Sm_2O_3 yield a maximum of 22%. Al_2O_3-Pr_6O_{11} produced an increase in yield to 16%. In the case of all other catalysts the

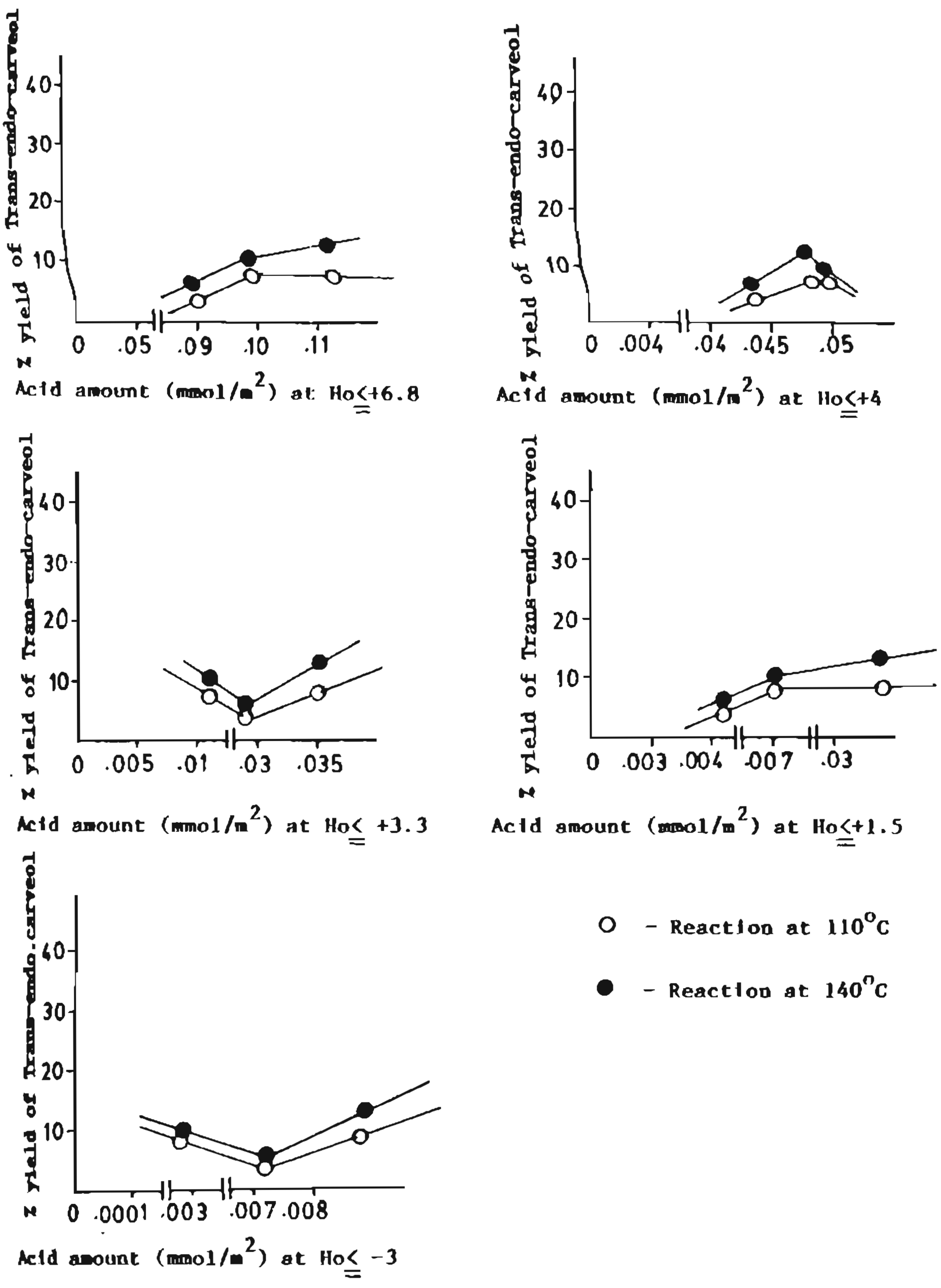


Fig.26 Variation in the percentage yield of Trans-endo-carveol with acid amount

percentage yield varied from 11 to 14. The mechanism of formation of carvone is illustrated in section 3.5.5.5.

From Fig.27 it is clear that as the acid amount at various strengths increased, the yield of carvone increased then decreased and again increased. So the variation in the percentage yield of carvone with acid amount in m mol/m^2 is not regular and no correlation can be obtained from the data.

3.6.7.5 8,(9)-p-menthene-1,2-diol (78)

At 110°C, Al_2O_3-Sm_2O_3 produced maximum yield of diol (46%) and over various other catalysts yield varied from 8 to 32%. Al_2O_3-Eu_2O_3 produced 32% diol and Al_2O_3-Pr_6O_{11} produced 30% diol.

As temperature changed to 140°C the yield of diol decreased over all catalysts except Al_2O_3-Y_2O_3. Al_2O_3-Y_2O_3 produced 8% diol at 110°C and 18% at 140°C. At 140°C maximum yield was observed over Al_2O_3-Y_2O_3 (18%). The formation of diol from tertiary carbonium ion is illustrated in section 3.5.5.6.

An attempt has been made to correlate the formation of diol with acidities at different Hammett acid strengths. Fig. 28 illustrates the variation of acid strength with percentage of diol at various acid amount. At 110°C there is an increase in yield of diol with acid amount at Ho $\leq$ +3.3.

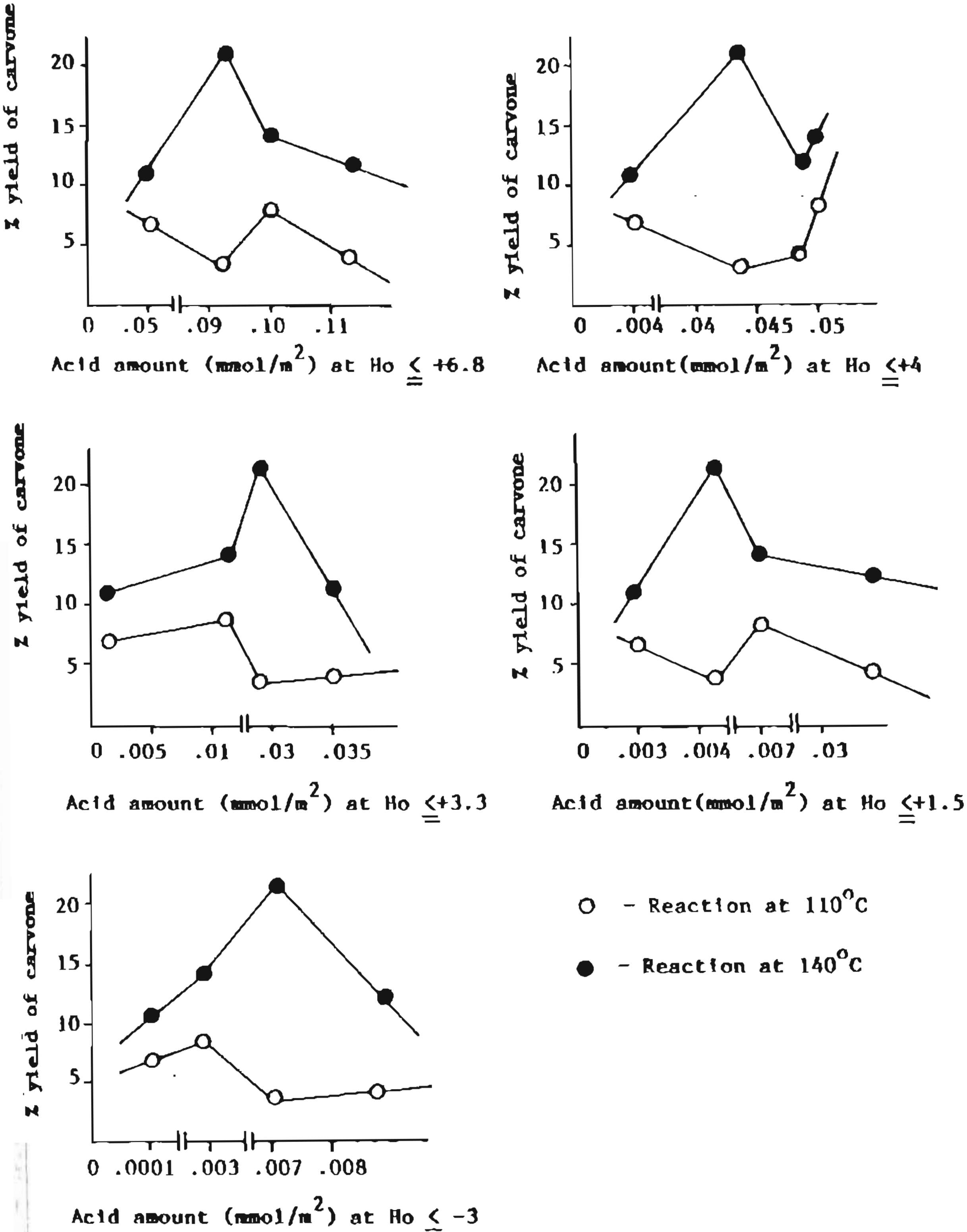


Fig. 27 Variation in the percentage yield of Carvone with acid amount

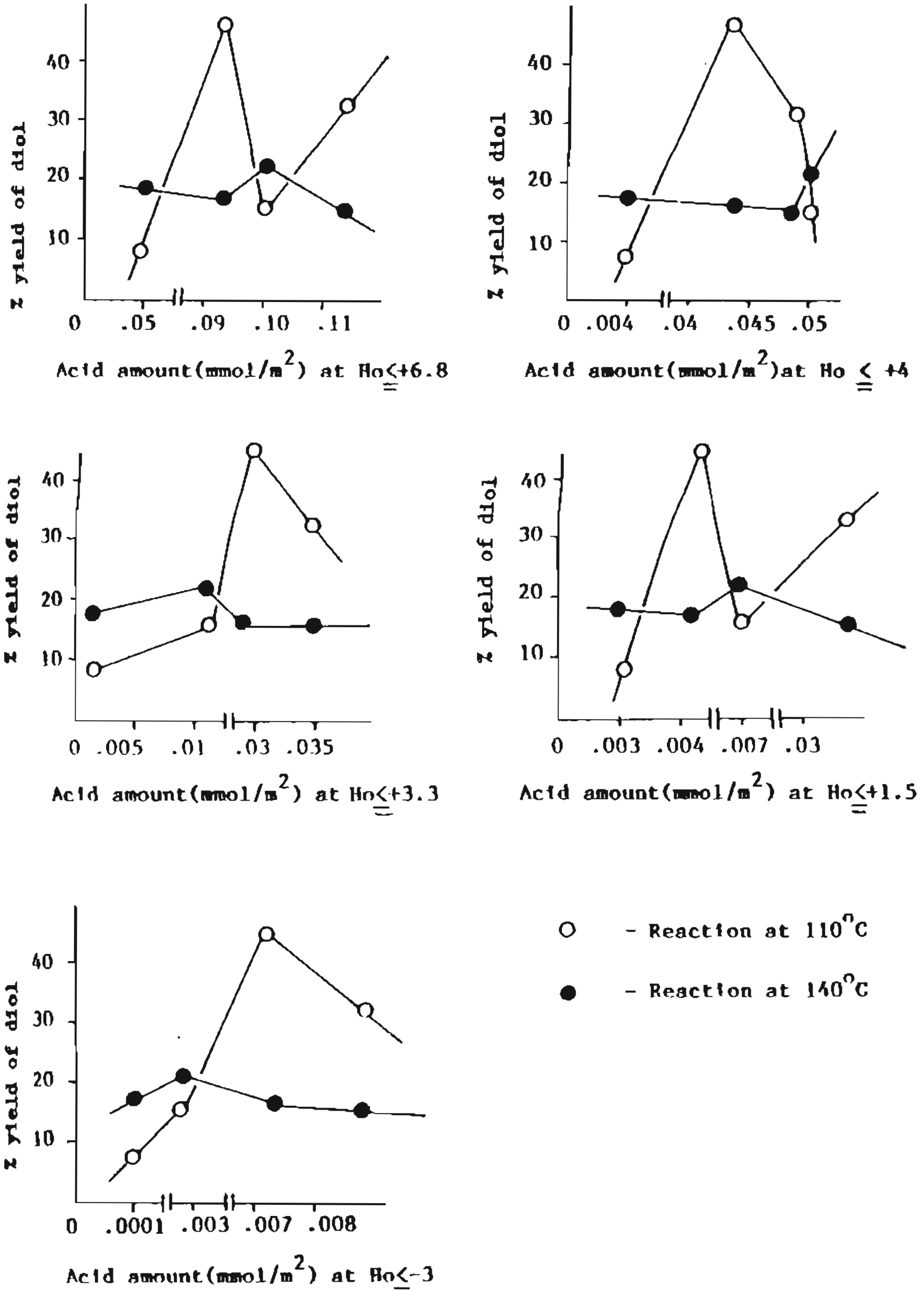


Fig. 28 Variation in the percentage yield of diol with acid amount.

At all other acid amounts there is no direct correlation for percentage production of diol and acidity.

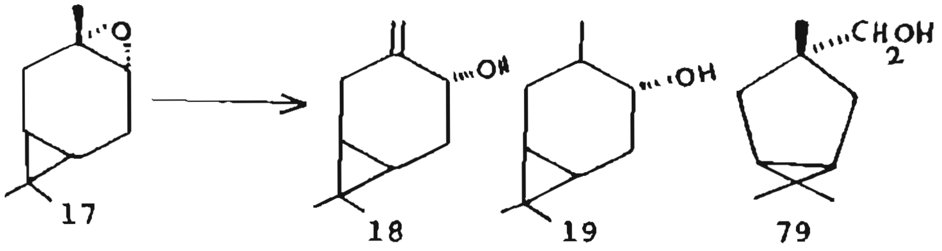
3.6.8 Comparison of the Reactivity of (+)-Limonene Oxide and (-)-Limonene Oxide

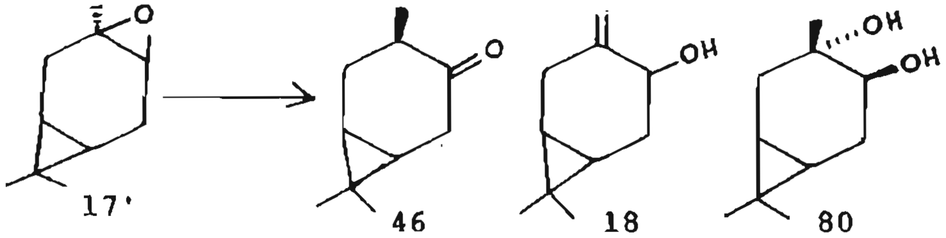
When reactivity of both isomers of limonene oxide were compared, (+)-limonene oxide showed more reactivity than (-)-isomer. Regarding selectivity more carbonyl compounds were produced over (+)-limonene oxide and all four isomers of allyl alcohols were formed. For (+)-isomer exo-allylic alcohol predominate over endo-allylic alcohols. In the case of (+)-limonene oxide, cis-endo-carveol is formed only over two catalysts. For (-)-isomer cis-endo-carveol is a major constituent in product mixture. Regarding diol formation, more diols were produced at 110°C than 140°C in the case of (-)-limonene oxide.

3.7 Transformations of 3-Carene Oxide [2,7,7 trimethyl 3-oxa tricyclo [4,1.0.0] octane] (17')

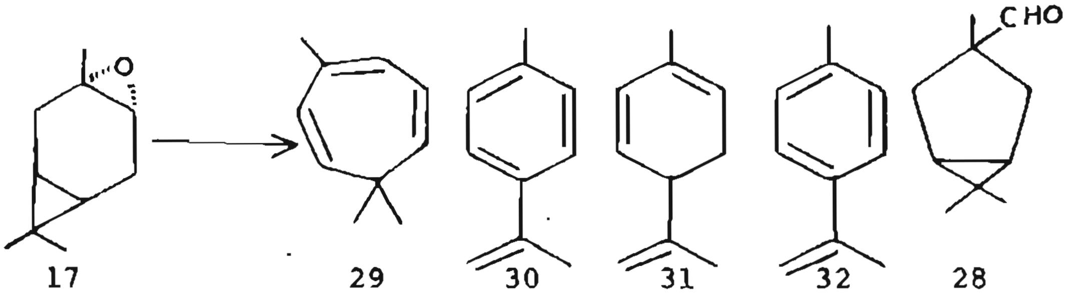
Earlier studies

Sukh Dev and co-workers studied the isomerization reactions of 3α, 4α epoxy carane and 3β ,4β expoxy carane over Al_2O_3 in hexane. They observed the formation of major amounts of alcohol in these reaction[87].



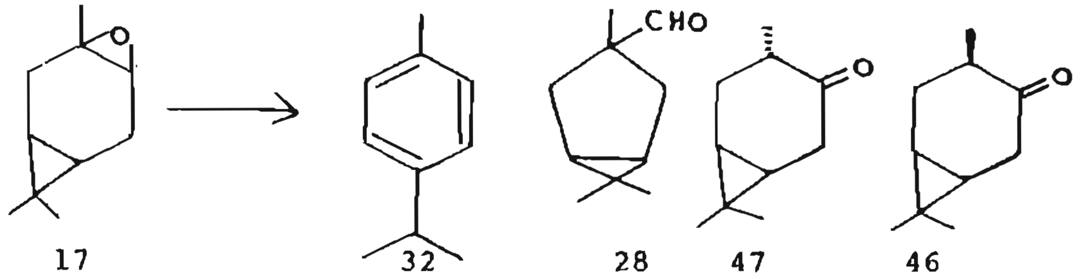


On contact with silica gel (+)- 3α, 4α epoxy carane (17) rearranged to give 3,7,7-trimethyl tropillidine (29) 1,methyl-4-isopropenyl benzene (30) 1,5,8 (9) p-mentha triene (31), p-cymene (32) and 3,6,6-trimethyl bicyclo (3.1.0) hexane-3-carbaldehyde[89] (28).

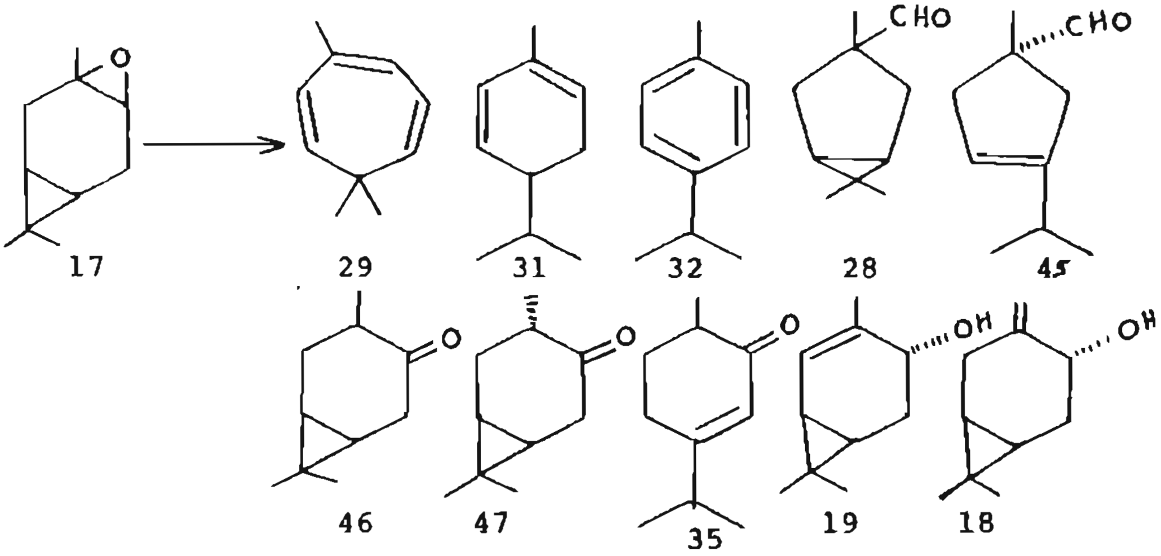


In the case of 3-carene oxide with alumina four different types of reactions were observed

(1) transformation in to allylic alcohol (2) hydration to a trans-glycol (3) isomerization to a ketone (4) typical carbonium ion rearrangements. Settine and co-workers observed the isomerization of 3-carene oxide over $ZnBr_2$ to p-cymene, an aldehyde, caranone and isocaranone.



As a part of their series of studies dealing with epoxide rearrangements, Tanabe and co-workers observed the following product formation from 3-carene oxide over catalysts like $NiSO_4$, $MgSO_4$, SiO_2-Al_2O_3, solid H_3PO_4 etc.[102,103].



The reaction products were 3,7,7-trimethyl tropilidine (29) 1,5,8(9)-p-mentha triene (31), p-cymene(32) 3,6,6-trimethyl bicyclo [3.1.0]hexane-3-carbaldehyde (28), methyl-1-formyl-3-isopropyl cyclopenta-3-ene(45) isocaranone (46), caranone (47), carvenone (35), trans-2-caren-4-01 (19) and trans-3(10), caren-4-01 (18).

The formation of various products depend on the nature of catalyst used. Acidic catalysts preferred carbonyl compounds and bifunctional catalysts preferred the formation of allyl alcohols. With H_2SO_4/SiO_2 the products formed resulted from the opening of three membered ring. Rare earth oxides like La_2O_3, Ce_2O_3 and Y_2O_3 are used for the isomerization of 3-carene. Binary oxides of alumina-rare earth oxides were not used in the isomerization studies of 3-carene oxide. So in the present study the author used binary oxides like Al_2O_3-Y_2O_3, Al_2O_3-Sm_2O_3, Al_2O_3-Pr_6O_{11}, Al_2O_3-Nd_2O_3 and Al_2O_3-Eu_2O_3.

3.7.1 Reactions of 3-Carene Oxide

Materials

(+)-3-carene (93% pure) supplied by Aldrich Chemical Company, U.S.A. Neutral Al_2O_3 suplied by Sisco. Solvents benzene and toluene were guaranteed reagents supplied by E. Merck (India) Ltd. Solvents were purified by distillation over sodium metal. Purity of (+) 3-carene was enriched to

97% by column chromatography over neutral Al_2O_3 and fractional distillation.

3.7.2 *Preparation of Monoperphthalic Acid*

Materials

Phthalic anhydride and 30% H_2O_2 supplied by E. Merck (India) Ltd. Phthalic anhydride was further purified by sublimation. Diethyl ether was obtained from BDH.

Drying of ether

Passed through a column containing neutral active Al_2O_3.$LiAIH_4$ added, kept for 24 hr and distilled and kept over sodium wire.

Experimental

Mono perphthalic acid was prepared by following the method of E.E. Royals and Harrell[96]. Freshly sublimed phthalic anhydride (60 g, 0.4 mol) and 100 ml 30% H_2O_2 and 400 ml dry ether were stirred together at a moderate rate at 20°C for 24 hr. After 24 hr the aqueous layer was separated from ethereal solution and washed with 150 ml portions of 40% ammonium sulphate solution. The solution was first dried with 30 g of anhydrous sodium sulphate and then over 45 g of drierite.

A 2 ml aliquot of the acid was added to 20 ml of 20% KI solution and titrated after 10 minutes. The liberated iodine was titrated against 0.1 M sodium thiosulphate solution. From the titre value, the weight of acid present per ml. was calculated.

3.7.3 Preparation of (+) 3-Carene Oxide (17')

50 g of (+) 3-carene (0.35 mol) was added in drop-wise to an ice cold solution of monoperphthalic acid and the reaction mixture was kept in a refrigerator till the reaction was complete. Completeness of reaction was monitored by TLC. The reaction mixture was filteared to remove the precipitated acid and extracted with ether. Ether solution was washed with saturated sodium bicarbonate solution to remove traces of free acid present. Ether solution was separated from aqueous phase and dried over anhydrous sodium sulphate. Solvent removed and traces of 3-carene present in the reaction mixture was removed by vacuum distillation. The epoxide obtained was 97% pure by GLC analysis. Yield 90%. The expodie is 1:1 mixture of cis and trans forms.

3.7.4 Reactions of 3-carene oxide

Reactions at 80°C

3-carene oxide (0.3 m mol), Al_2O_3-Y_2O_3(1 g) and 5 ml solvent (benzene) were stirred at 80°C. Percentage conversion of reactant was monitored by TLC at 20 minute intervals. After 1 hr the reaction was found to be slow.

Reaction mixture was filtered and catalyst extracted with methylene chloride. All extracts combined together and solvent removed in vacuum. All five binary oxide catalysts were used for the study.

Reactions at 110°C

Reactions at 110°C were done similarly as reactions at 80°C. The same procedure was followed for all binary oxide catalysts.

3.7.5 Preparation of Authentic Samples

3.7.5.1 Preparation of 3,6,6-Trimethyl bicyclo [3.1.0] hexane carboxaldehyde (28)

Materials

3-carene oxide, zinc bromide, dry benzene.

Experimental

The procedure followed was the method of R.L.Settine and co-workers[160]. To a refluxing solution of zinc bromide in 50 ml of dry benzene was added slowly to a solution containing 10.85 g (0.071 mol) of 3-carene oxide in 50 ml of dry benzene. An exothermic reaction was followed which was controlled by placing the reaction vessel in a water bath. The reaction mixture was then refluxed for 2 hr, cooled and 500 ml water added. The benzene solution was separated from aqueous layer and washed with H_2O to remove traces of zinc salts and benzene layer dried over anhydrous sodium sulphate. Solvent was removed. The crude material obtained was fractionally distilled in vacuum. The 2nd fraction collected at 70-80°C (10 mm of Hg) was a mixture of aldehyde and ketones. The constituents were identified by GLC analysis as 3,6,6-trimethyl bicyclo [3.1.0] hexane carboxaldehyde and carnone and isocaranone. Total yield 7.5 g (69%) IR, NMR of the mixture was taken. Purity of the product was 87% by GLC analysis.

3.7.5.2 Preparation Trans-3(10) caren-4-ol (18)

Materials

3-carene oxide, Aluminium isopropoxide. The procedure used by E.H. Eschinasi[99] was adopted.

Experimental

A mixture of 32 g (0.210 mol) of 3-carene oxide and 30 g of aluminium isopropoxide were slowly heated in coarse vacuum (150 mm Hg). The reaction temperature rose to 150°C and a mixture of allylic alcohol distills over. The mixture containing four allylic alcohols were separated in GLC. Yield of trans-3 (10)-caren-4-ol was 26% and purity was 86% by GLC analysis.

3.7.5.3 Preparation of Caran-diol (80)

Materials

3-carene oxide, THF and 1% H_2SO_4.

Experimental

The procedure followed was given by Arbuzov[158]. The diol was prepared by following the same procedure as given in section 3.5.3.3. The yield of diol was 70% with purity 81% by GLC analysis.

3.7.5.4 Preparation of Trans-Caran-3-ol (81)

Materials

3-carene, THF, diborane solution in THF supplied by Aldrich Chemical Company. NaOH solution, 30% H_2O_2, diethyl ether and dry $MgSO_4$.

Experimental

The method followed is the procedure given by H.C. Brown et al.[161]. 3-carene (4 g, 150 m mol) was taken in a three necked flask which was equipped with a thermometer, condensor and a pressure equalising funnel. To the flask THF (60 ml) was added. Reaction mixture was cooled to 0°C and with stirring diborane solution in THF (35.7 ml) was added drop-wise. The mixture was stirred at 0°C for 3 hr. Water (7.5 ml) in 15 ml THF was added drop-wise for 30 minutes. After the addition of water, reaction mixture was allowed to stand for 1 hr. During the period H_2 was evolved. To the resulting mixture, NaOH (3N, 18 ml) was added followed by 18 ml of 30% H_2O_2 in drops for 15 minutes. Reaction temperature was carefully maintained at 45°C. Reaction mixture was stirred for another 3 hr at room temperature. The alcohol formed in the reaction was extracted three times with ether and ether extracts were combined together and dried over drierite. The reaction mixture was distilled in vacuum to remove solvent and the fraction collected at 89°C (35 mm Hg) was the alcohol. Yield 63% and purity was 90% by GLC analysis.

3.7.6 Identification of Products

The reaction products were analysed by GLC, GC-MS and constituents were identified by comparing relataive retention time with authentic sample. Linalyl acetate was used as the internal standard. The percentage of individual constituents were calculated from the area percentage data produced by the electronic integrator of the GLC. Mass spectral data given is in the decreasing order of abundance.

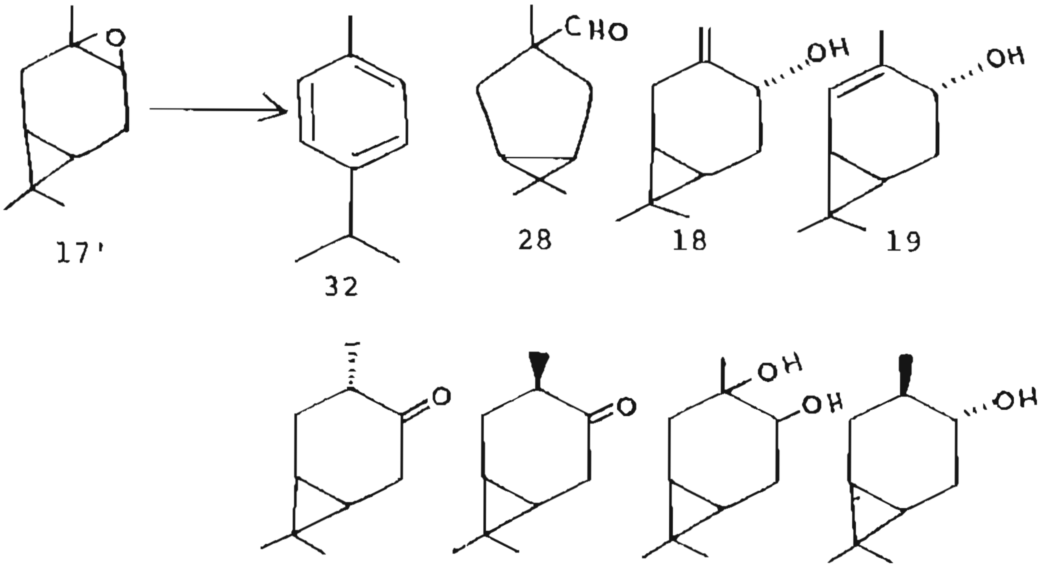
Compound 32 was identified as p-cymene by comparing its RRT with authentic sample supplied by Fluka A.G. Chem U.S.A. and MS.

119(100), 91, 41, 77, 65, 51, 58, 103, 134, 74.

Compound 28 was identified as 3,6,6-trimethyl bicyclo [3.1.0] hexane carboxaldehyde by its RRT, with authentic sample and MS.

41(100), 67, 81, 109, 55, 91, 137, 123, 119, 152.

conversion. Al_2O_3-Nd_3O_3 produced 10% conversion to products.



17'

32

28

18

19

47

46

80

81

At 110°C the yield over various catalysts ranged from 50 to 92%. Maximum conversion 92% was observed over Al_2O_3-Pr_6O_{11}. Al_2O_3-Sm_2O_3 produced 88% conversion while Al_2O_3-Nd_2O_3 produced only 50%.

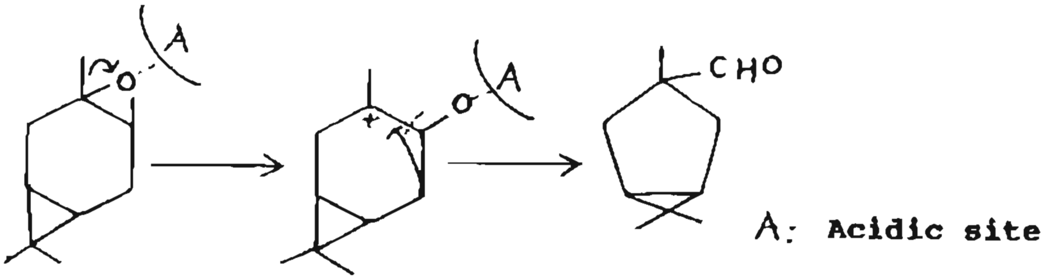
Catalysts like Al_2O_3-Y_2O_3, Al_2O_3-Sm_2O_3, Al_2O_3-Nd_2O_3, Al_2O_3-Pr_6O_{11} and Al_2O_3-Eu_2O_3 transformed -3-carene oxide (17') to the following products. P-cymene (32), 3,6,6-trimethyl bicyclo[3.1.0] hexane-3-carboxaldehyde(28), 3(10)-caren-4-ol(18), trans-2-caren-4-01(19), caranone (47), isocaranone (46), caran diol (80) and trans-caran-3-01 (81). In the isomerization reaction carbonyl compounds were the major products obtained.

3.7.7.2 3,6,6-Trimethyl bicyclo [3.1.0] hexane-3-carboxaldehyde (28)

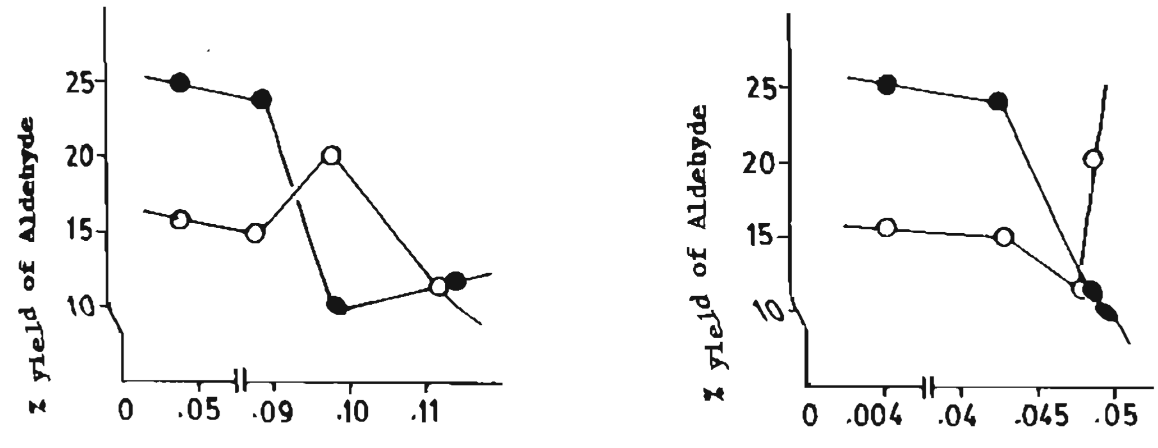
The percentage yield of aldehydes varied from 12 to 24 at 80°C over various catalysts. Al_2O_3-Pr_6O_{11} produced maximum yield of 24%. Al_2O_3-Y_2O_3 produced 16% aldehyde while Al_2O_3-Sm_2O_3 produced only 15%. Al_2O_3-Nd_2O_3 produced 20% aldehyde.

At 110°C, Al_2O_3-Y_2O_3 and Al_2O_3-Sm_2O_3 produced an increased yield of aldehyde, while other catalysts showed a decrease in yield. Al_2O_3-Y_2O_3 produced maximum yield of 25% followed by Al_2O_3-Sm_2O_3 (24%).

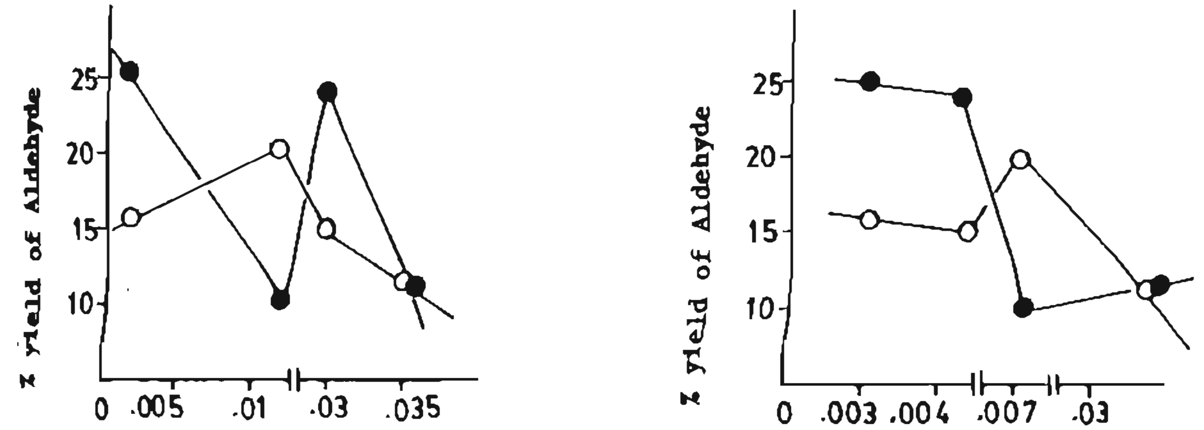
The formation of aldehyde can be explained as below. The epoxide gets adsorbed on the catalyst surface through oxygen atom and epoxide ring opens up followed by a ring contraction to form aldehyde.



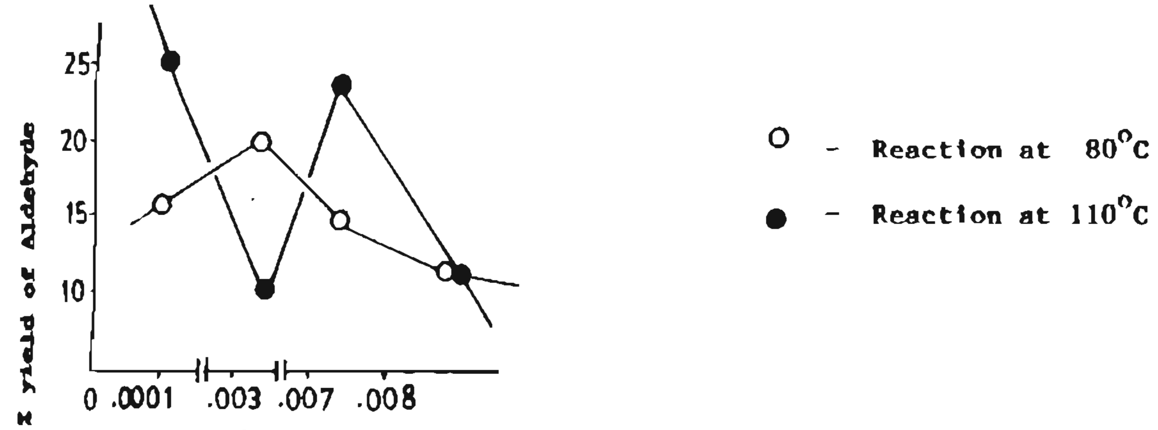
An attempt has been made to correlate the acidic and basic amounts with percentage yield of aldehyde. Fig.29 gives the correlation of acid amount in m mol/m^2 at different acid strength. Thre was no specific correlation



Acid amount (mmol/m^2) at Ho $\leqq$ +6.8 Acid amount(mmol/m^2) at $H_o \leqq$ +4



Acid amount (mmol/m^2) at Ho $\leqq$ + 3.3 Acid amount(mmol/m^2) at Ho $\leqq$ +1.5



Acid amount(mmol/m^2) at Ho $\leqq$ -3

Fig.29 Variation in the percentage yield of 3,6,6-Trimethyl bicyclo [3.1.0] hexane carboxaldehyde with acid amount.

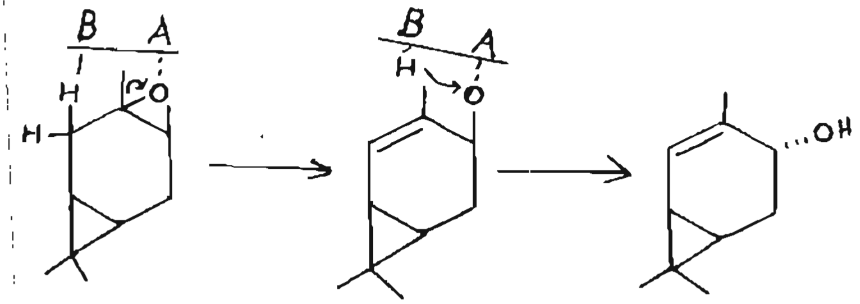
observed at different temperatures and hence useful conclusions could not be obtained.

3.7.7.3 Trans-2-caren-4-Ol,[3,7,7-Trimethyl bicyclo [4.1.0] hept-2-ene-4-ol] (19)

The yield of trans-2-caren-4-Ol varied from 9 to 30% at 80°C over various alumina-rare earth oxide catalysts. Maximum 30% yield was obtained over Al_2O_3-Nd_2O_3 while 16% yield was obtained over Al_2O_3-Sm_2O_3. Al_2O_3-Pr_6O_{11} produced 13% trans-2-caren-4-ol and 9% product obtained over Al_2O_3-Y_2O_3.

At 110°C the yield ranged 11, 10 and 12% over Al_2O_3-Eu_2O_3, Al_2O_3- Y_2O_3 and Al_2O_3-Sm_2O_3 respectively.

The formation of alcohol can be illustrated by the adsorption of epoxide oxygen on catalyst surface on an acidic site with the opening of epoxide ring resulting a tertiary carbonium ion. A proton from ring carbon is extracted by a basic site, which results an unsaturation in the ring. Proton migrates to oxygen forming an alcohol.



A : Acidic site B : Basic site

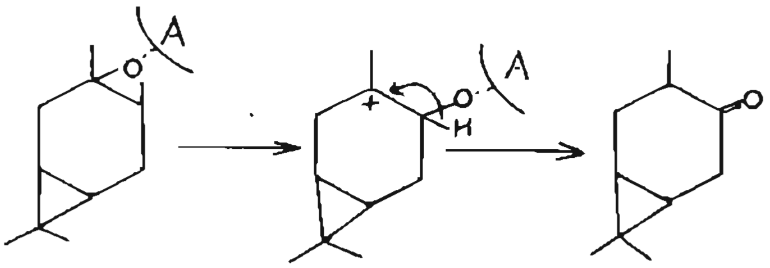
A correlation has been attempted for acidic and basic amounts with percentage yield of alcohol production. The variation of yield with acid amounts is irregular and no correlation can be obtained as evident in Fig.30 at all acid strengths except $Ho \leqq -3$. At $Ho \leqq -3$ as acid strength increased, a gradual increase in the yield of alcohol was observed at 110°C.

3.7.7.4 Caranone [3,7,7-Trimethyl bicyclo [4.1.0] hept-4-one] (47)

The yield of caranone varied from 11 to 30% over various catalysts.Al_2O_3-Nd_2O_3 produced maximum yield of 30%, while 24% yield obtained over Al_2O_3-Sm_2O_3. At 80°C the lowest yield 11% was observed over Al_2O_3-Y_2O_3.

At 110°C, 45% yield was obtained over Al_2O_3-Eu_2O_3 and 15%, over Al_2O_3-Y_2O_3. Al_2O_3-Nd_2O_3 produced no caranone.

The formation of ketone from epoxide takes place by transfer of a proton from carbon bearing oxygen atom to tertiary carbonium ion formed by the opening of epoxide ring after adsorption to the catalyst surface.



A : Acidic site

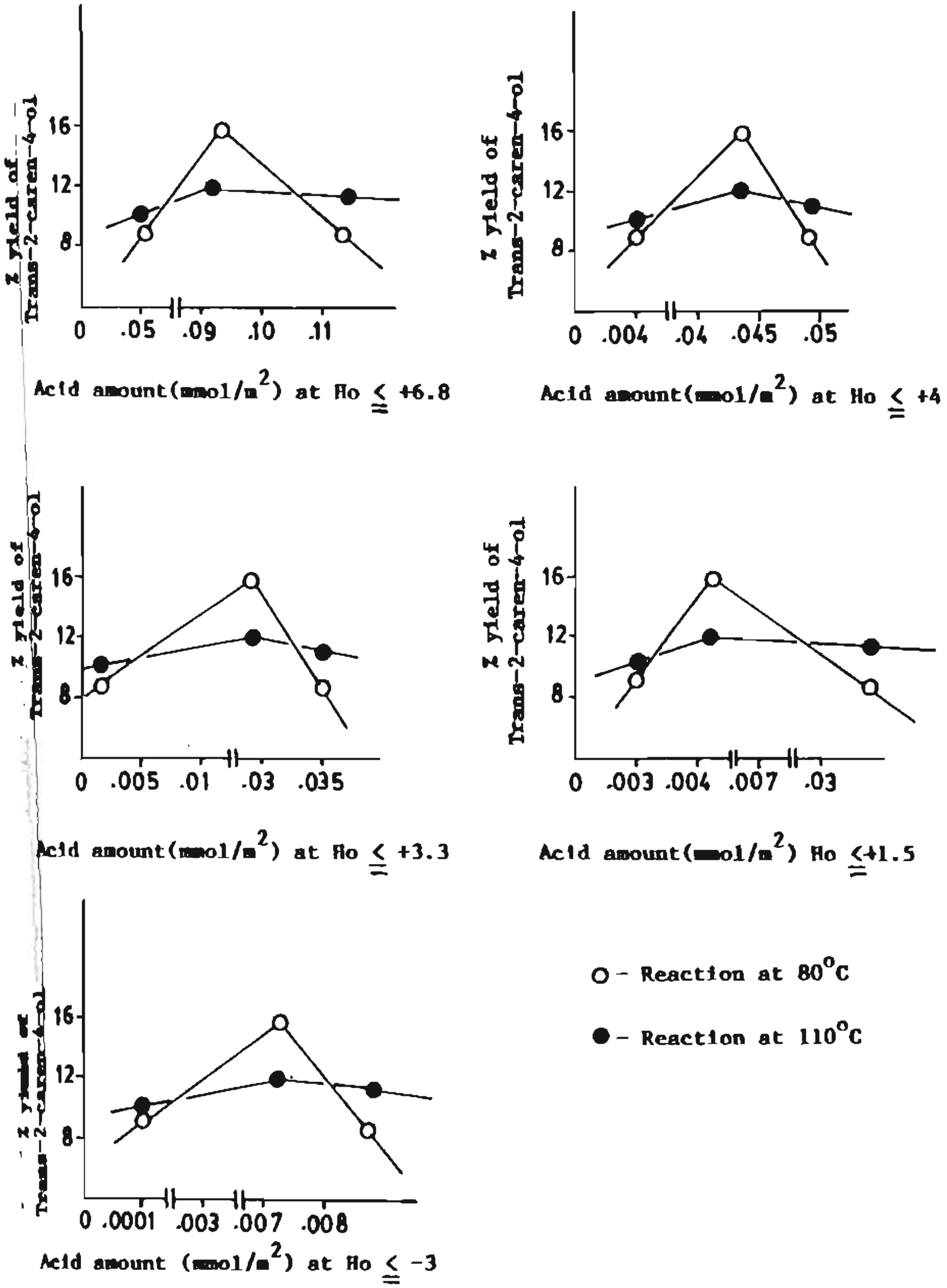


Fig.30. Variation in the percentage yield of Trans-2-caren-4-ol with acid amount.

The variation in the yield of caranone with acidities at various acid strength are depicted in Fig.31. As evident from Fig. 31, there is no regular variation in the yield of caranone with acidity at various acid strength and hence no useful correlation is obtainable.

3.7.7.5 Trans-caran-3-ol [3,7,7-Trimethyl bicyclo [4.1.0] heptan 4-ol (81)]

At 80°C, the yield of trans-caran-3-ol varied from 3 to 15% over various catalysts. Maximum yield was observed over Al_2O_3-Sm_2O_3 and 13% yield obtained over Al_2O_3-Pr_6O_{11}. As temperature increased to 110°C, yield of alcohol increased in the case of Al_2O_3-Pr_6O_{11}, Al_2O_3-Eu_2O_3 and Al_2O_3-Nd_2O_3. Al_2O_3-Nd_2O_3 produced 25% alcohol, while 22% was produced by Al_2O_3-Pr_6O_{11}.

The formation of trans-caran-3-ol can be illustrated as follows. The epoxide gets itself attached to the acidic site on the surface of catalyst by weak attractive forces through oxygen atom. The epoxide ring opens up resulting in the formation of a tertiary carbonium ion which abstracts a proton from catalyst's surface to yield an alcohol.

In Fig. 32, an attempt is made to correlate acid amounts at various Ho values and percentage yield of trans-caran-3-ol. As evident from Fig. 32 there is no direct

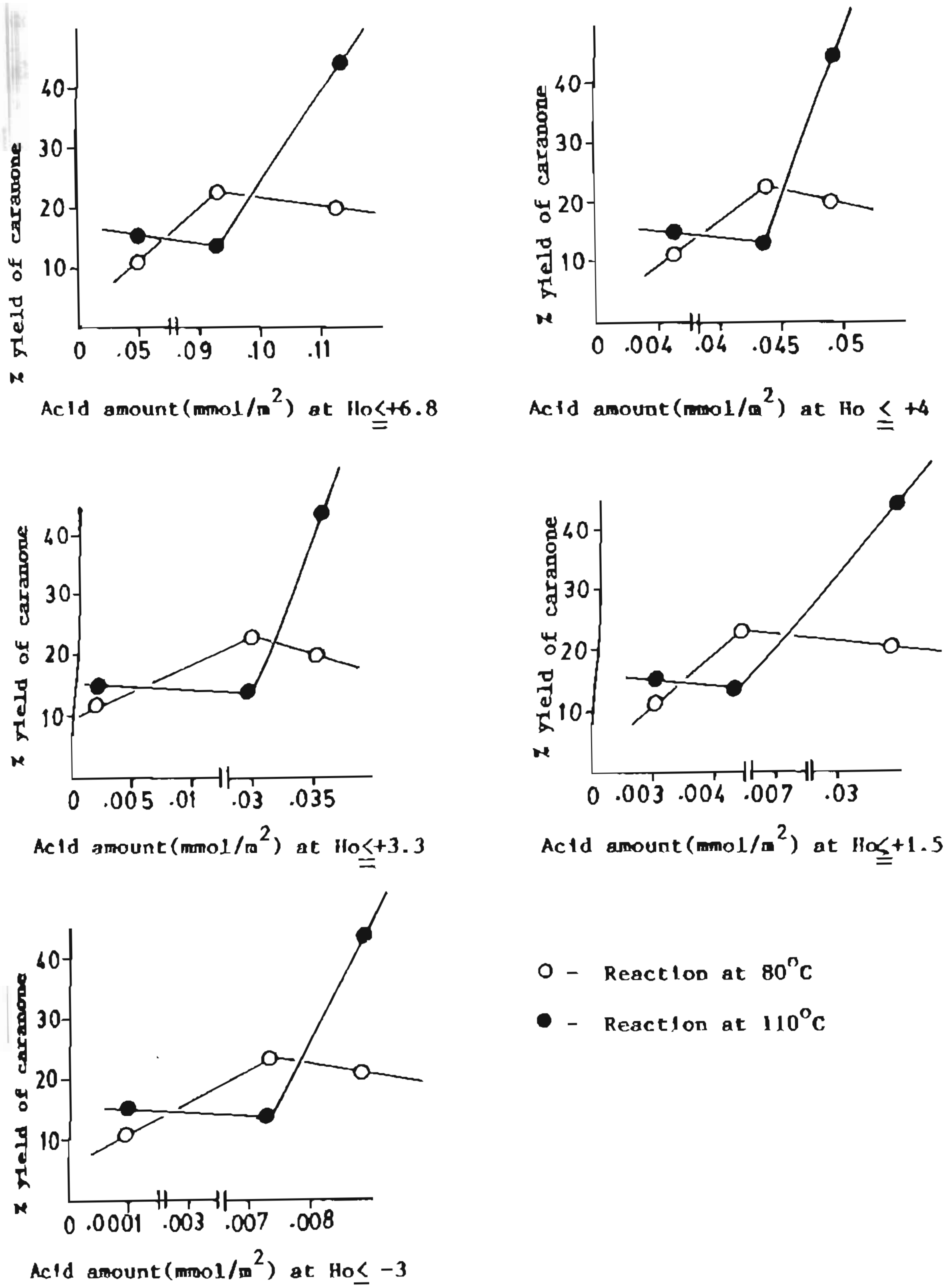
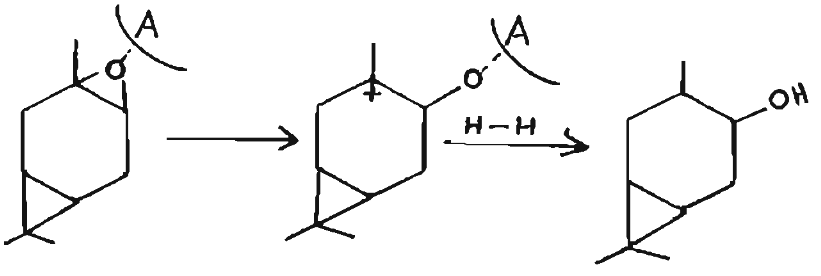


Fig.31 Variation n the percentage yield of caranone with acid amount

correlation for the variation of acid amount and yield of alcohol.



A : **Acid site**

Along with major products mentioned above, small amounts of trans-3-caren-4-ol (18), isocaranone (48) caran diol (80) were obtained in minor amounts as shown in table 28 and 29.

Table 28

Activity of Catalysts in the Transformation of 3-Carene Oxide in Benzene

Catalysts 1:1	Conversion (%)	Products %							
		32	28	18	19	47	48	80	81
Al_2O_3-Y_2O_3	44	-	16	-	9	11	10	43	3
Al_3O_3-Pr_6O_{11}	38	-	24	-	13	15	8	18	13
Al_2O_3-Sm_2O_3	46	3	15	-	16	24	6	-	15
Al_2O_3-Eu_2O_3	32	3	12	16	9	20	-	-	5
Al_2O_3-Nd_2O_3	10	-	20	-	30	30	-	-	10

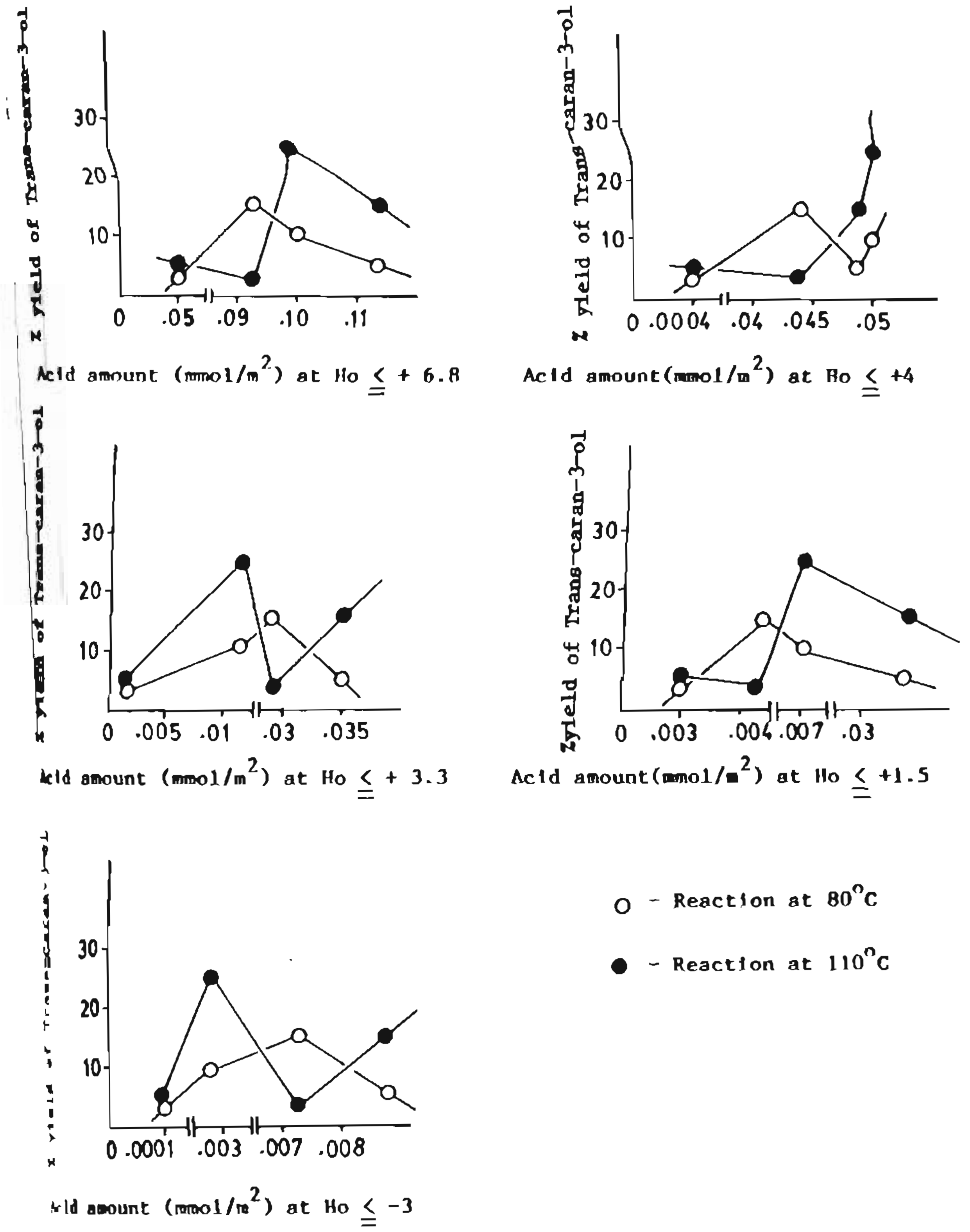


Fig.32 Variation in the percentage yield of Trans-caran-3-ol with acid amount

Table 29

Activity of Catalysts in the Transformation of 3-Carene Oxide in Toluene

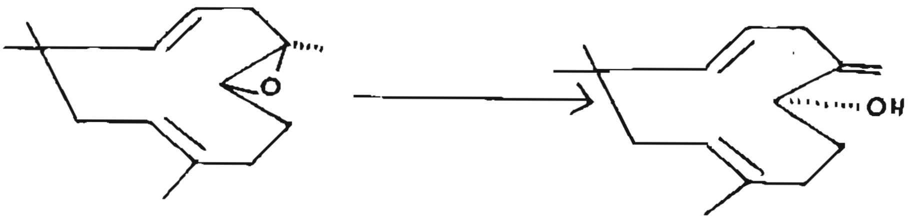
Catalyst 1:1	Conversion %	Product %							
		32	28	18	19	47	48	80	81
Al_2O_3-Y_2O_3	60	-	25	-	10	15	5	22	5
Al_3O_3-Pr_6O_{11}	92	5	21	-	10	12	-	-	22
Al_2O_3-Sm_2O_3	88	5	24	-	12	13	-	1	3
Al_2O_3-Eu_2O_3	70	3	12	-	11	45	-	-	15
Al_2O_3-Nd_2O_3	50	4	10	25	-	-	-	-	25

3.8 Transformations of Ar-curcumene Epoxide

3.8.1 Earlier Studies

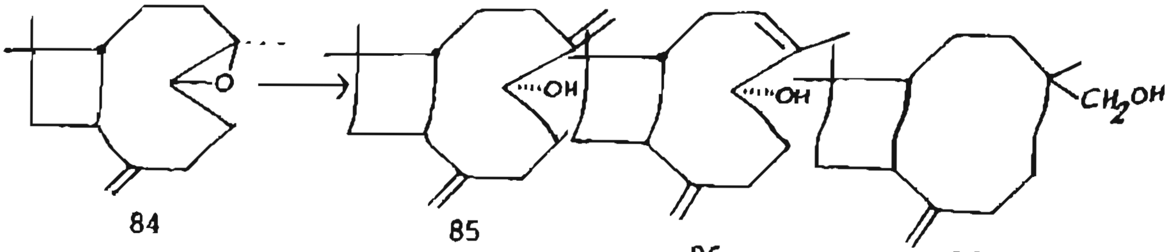
There are very few reports on the transformation studies of sesquiterpene epoxides on oxide catalysts and studies on ar-curcumene epoxide has not been reported. The few reports on humulene epoxide and caryophyllene epoxide are given briefly below.

Nigam and Levi[162] while working on the isolation and purification of humulene epoxide observed the transformation of epoxide to alcohol on alumina.



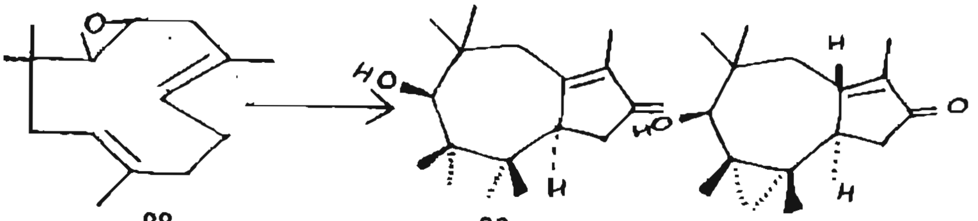
82 83

Similarly caryophyllene oxides (84) in petroleum ether at room temperature yielded three allylic alcohols in 70, 21, and 9% yields on Al_2O_3.[85,163,164]



84 85 86 87

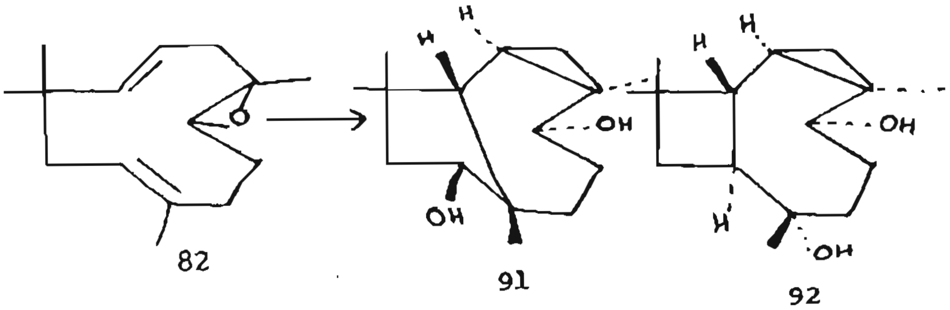
Robert et al.[165] observed the rearrangement of humulene 4,5 epoxide (88) with BF_3-etherate to two tricyclic alcohols.



88 89 90

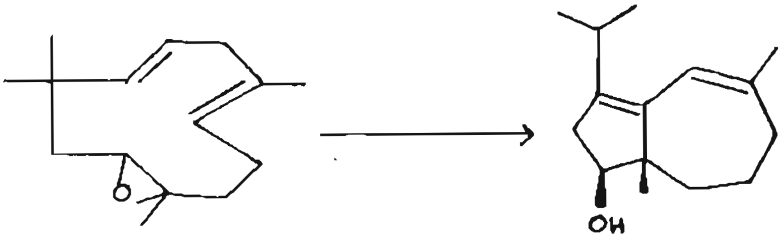
1.2 humulene epoxide in presence of acid catalysts

rearranges to tricyclic diols[166,167]



82 91 92

In 1980, Roberts and co-workers obtained a bicyclic alcohol from humulene -8,9 epoxide with tin chloride in $CHCl_3$ solution at -15°C for 15 minutes reaction.[168]



93 94

3.8.2 Preparation of Ar-curcumene [Benzene, 1-(1', 5'-dimethyl -4' hexenyl)-4 methyl]

Materials

Zingiberene, 2,3-dichloro 5,6-dicyano 1,4-benzoquinone supplied by Sigma Chemie and benzene. Zingiberene was isolated from hydrocarbon fraction of ginger oil by fractional distillation under vacuum.[169]

Experimental

Ar-curcumene was prepared by the method of Menon.N. et al.[170]. 25 g of Zingiberene (95) in 20 ml dry benzene *refluxed with 23 g of 2,3 dichloro 5,6 dicyano* 1,4-benzoquinone for 1 hr. After 1 hr, reaction mixture filtered and solvent removed. Reaction mixture was purified by column chromatography over neutral Al_2O_3. The IR and NMR of ar-curcumene was found to be comparable to the reported data. GLC analysis of sample recovered showed 60% yield and 90% purity.

3.8.3 Preparation of Ar-curcumene Oxide [Benzene,1-(1',6'-dimethyl -4' oxaheptane) -4 methyl] (97)

Materials

Ar-curcumene, *monoperphthalic acid, ether.*

Experimental

Ar-curcumene 50 g (0.246 mol) was slowly added to monoperphthalic acid kept at 0°C in an ice bath. The reaction mixture was kept in refrigeratoar till the reaction is complete. Reaction mixture filtered and filtrate washed with aqueous sodium bicarbonate solution. The solution was dried over anhydrous sodium sulphate and solvent removed. Reaction mixture purified by column chromatography on Al_2O_3. Purity of the epoxide was found to be 90% by GLC analysis IR, NMR of the epoxide was taken.

IR:2980, 2880, 1620, 1460, 1380, 1120, 820 cm^{-1}

NMR ($CHCl_3$) ppm : 4H (unresolved m at 6.9, $-C_6\underline{H}_4-$), 3H(S, at 2.25, $C_6H_4-C\underline{H}_3$), 1H (unresolved S at 1.4, $C_6H_4-\overset{|}{C}\underline{H}-$), 3H (m at 1.3, $C_6H_4-\underset{|}{C}-C\underline{H}_3$) 3H (m at 1.2, $\overset{O}{C\text{--}C}-C\underline{H}_3$), 3H (m at 1.15 - $\overset{O}{C\text{-}C}-C\underline{H}_3$)

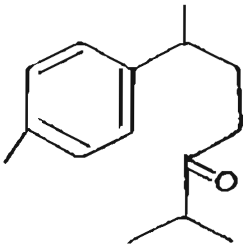
3.8.4 Reactions of ar-curcumene epoxide

Experimental

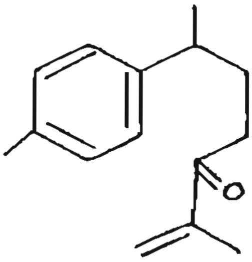
500 mg (2 m mol) of epoxide was mixed with 2.5 g of catalyst and 10 ml solvent (toluene) and stirred under reflux. Reaction rate was monitored by TLC. After 8 hr, reaction was found to be slow. Catalyst separated by filteration and extracted with methylene chloride. All extracts combined together and solvent removed. Reaction mixture was purified by column chromatography on neutral alumina. Two main fractions separated and solvent removed. The same reaction procedure was followed over all other catalysts.

3.8.5 Identification of Products

Infra red spectrum of fraction 1 showed absorptions at 1725 cm^{-1}, 1670 cm^{-1} showing it to be a mixture of saturated and α, β unsaturated ketones in the proportion of 3:1 approximately. Fraction 1 showed single spot in TLC (petroleum ether, 60-80°C solvent system). The NMR spectrum gave indication that this to be a mixture of benzene-1-(1',5'-dimethyl hexen-4'-one) -4 methyl and benzene-1 (1',5' dimethyl 5'-hexan-4'-one)-4 methyl. The mixture of two ketones could not be separated.



98

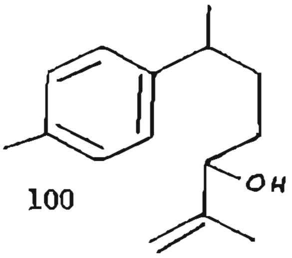


99

Fraction II showed infrared absorptions for hydroxyl at 3400 cm^{-1} and olefinic protons ($> C=CH_2$) at 890 cm^{-1}.

The NMR ($CHCl_3$) showed, 4H (unresolved m at 6.8, $-C_6\underline{H}_4-$), 1H (d, at 4.7, $C = C\underline{H}_2$), 1H(d, at 4.6, $C = C\underline{H}_2$), 1H (m, at 3.8, $-CH_2-\overset{|}{C}\underline{H}-OH$), 1H (unresolved m at 3,$-\overset{|}{\underset{|}{C}}H-O\underline{H}$), 3H(S, at 2.2 $C_6H_4-C\underline{H}_3$). 3H(unresolved m at 1.5, $=\overset{\backslash}{C}-C\underline{H}_3$) 3H (S, at 1.2, $-\overset{|}{\underset{|}{C}}-\overset{|}{C}H-C\underline{H}_3$) 1H(unresolved m at 1.1, $-\overset{|}{\underset{|}{C}}-\overset{|}{C}\underline{H}-CH_3$)

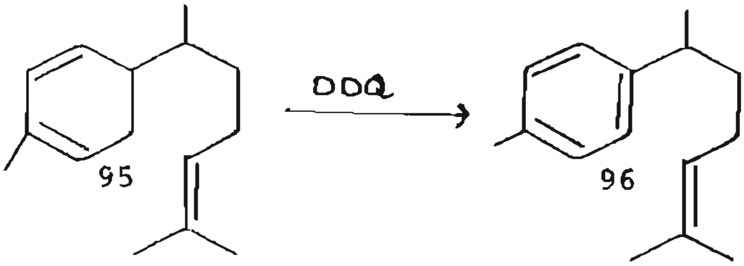
Based on the above spectral data fraction 11 was identified as benzene -1(1',5'-dimethyl 5'-hexen-4'-ol) -4 methyl (100).



100

3.8.6 Results and Discussion

Nuciferol is a widely used perfumery chemical in cosmetic industry. Ar-curcumene, the starting material for ar-curcumene oxide was obtained from Zingiberene as shown in scheme 2.



Scheme 2

Zingiberene constituted about 30-35% in ginger oil. A process has been developed in our laboratory for de-terpenation of ginger oil by column chromatographic procedure over silica gel. The hydrocarbon fraction was fractionated under vacuum to obtain zingiberene in approximately 60% purity. The zingiberene fraction was subjected to DDQ reaction and the product subjected to elaborate column chromatography to obtain ar-curcumene in

90% purity. Ar-curcumene oxide was prepared by monoperphthalic acid and product purified by column chromatography. By GLC analysis it was found to be 90% pure.

The ar-curcumene oxide was subjected to catalytic reaction with various alumina rare earth oxide catalysts. The conversion rate of ar-curcumene oxide was calculated based on the ar-curcumene oxide recovered during the column chromatographic purification of the product.

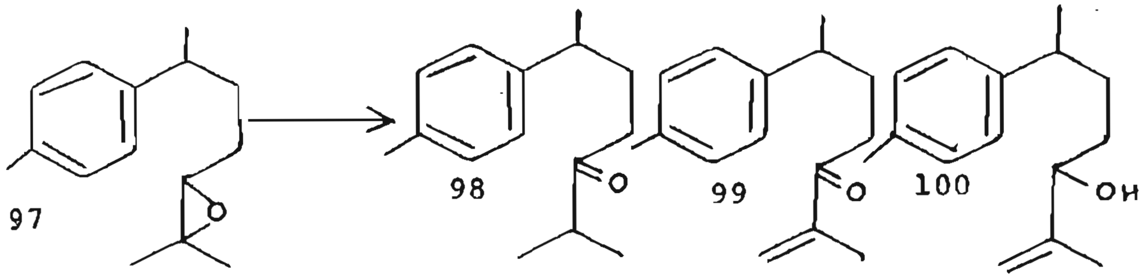
Table 30 gives the activity and selectivity of various catalysts for the isomerization of ar-curcumene oxide. At 110°C ar-curcumene oxide rearranges to ketones 98, 99 and allylic alcohol 100. The ketones 98 and 99 could not be separated by column chromatography and hence it is reported together as percentages of products in the table.

Table 30

Activity and Selectivity of Various Catalysts for Transformation of Ar-curcumene Oxide

Catalyst	Conversion %	Product %	
		98 and 99	100
Al_2O_3-Y_2O_3	65	10	50
Al_2O_3-Sm_2O_3	80	10	60
Al_2O_3-Eu_2O_3	90	15	70
Al_2O_3-Nd_2O_3	85	12	68
Al_2O_3-Pr_6O_{11}	63	8	55

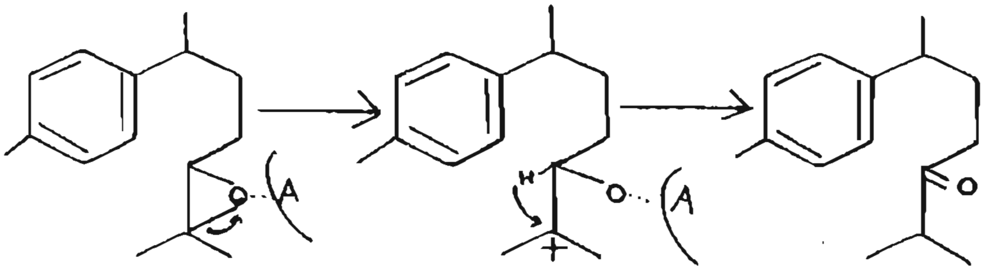
The percentage conversion over various catalysts varied from 63 to 90. Al_2O_3-Eu_2O_3 produced maximum conversion (90%) and 85% conversion was observed over Al_2O_3-Nd_2O_3. Al_2O_3-Sm_2O_3 produced 80% conversion to products.



3.8.6.1 Benzene-1-(1',5' dimethyl-hexan-4'-one)-4 methyl and Benzene-1 (1',5' dimethyl-5'hexen-4'-one)-4 methyl (98,99)

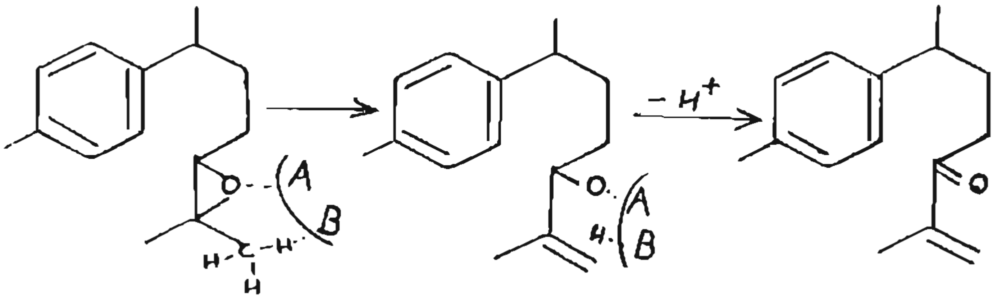
Over various catalysts the yield of ketones varied from 8 to 15%. Maximum ketones were produced over Al_2O_3-Eu_2O_3 (15%). Al_2O_3-Y_2O_3 and Al_2O_3-Sm_2O_3 produced 10% ketones.

The formation of ketones are pictured as below. The epoxide gets adsorbed on the acidic site on catalyst surface. The epoxide ring opens up forming a tertiary carbonium ion which abstracts a proton from carbon bearing C-O bond to give a saturated ketone.



A : **Acidic site**

The formation of unsaturated ketone is depicted as follows. The epoxide attaches itself to the surface of the catalyst through oxygen atom by weak electro static forces. Epoxide ring opens up forming a tertiary carbonium ion and a proton is abstracted by a basic site which eliminates a proton to give unsaturated ketone.

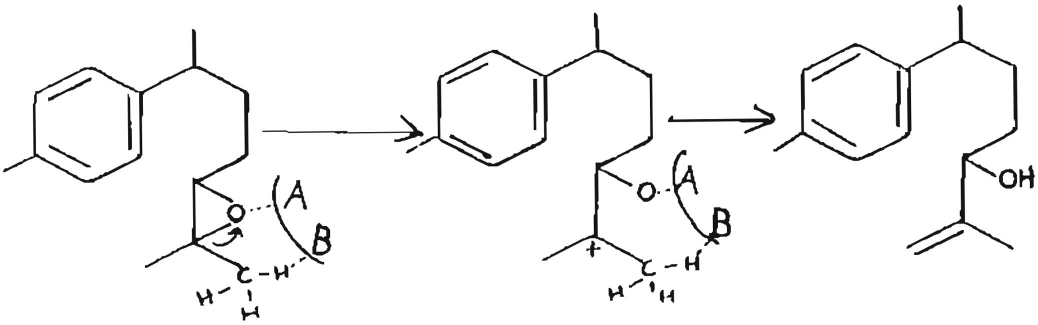


A : **Acidic site** B : **Basic site**

3.8.6.2 Benzene -1-(1',5'-dimethyl-5'-hexen-4'-ol)-4 methyl (100)

The percentage yield of alcohol varied from 50 to 70 over various catalysts. Al_2O_3-Eu_2O_3 produced 70% alcohol, while 68% was produced over Al_2O_3-Nd_2O_3. Al_2O_3-Sm_2O_3 produced 60% of alcohol.

The formation of alcohol from epoxide can be explained with the bifunctional nature of catalyst. Epoxide gets attached to an acidic site on catalyst surface, through oxygen atom and epoxide ring opens up forming a tertiary carbonium ion. A proton from the methyl group is abstracted by a basic site on catalyst surface. The proton gets transferred to oxygen atom to form alcohol.



A: **Acidic site**   B: **Basic site**

An attempt to correlate the acid strength with percentage yield of alcohol is made in Fig.33. The yield of alcohol increased with the increase in acid amount at Ho $\leq$ +6.8, +4 and +1.5. A similar observation can be made for basicity value at pKBH +15. Thus there exists a correlation between percentage yield of alcohol, acidity and basicity.

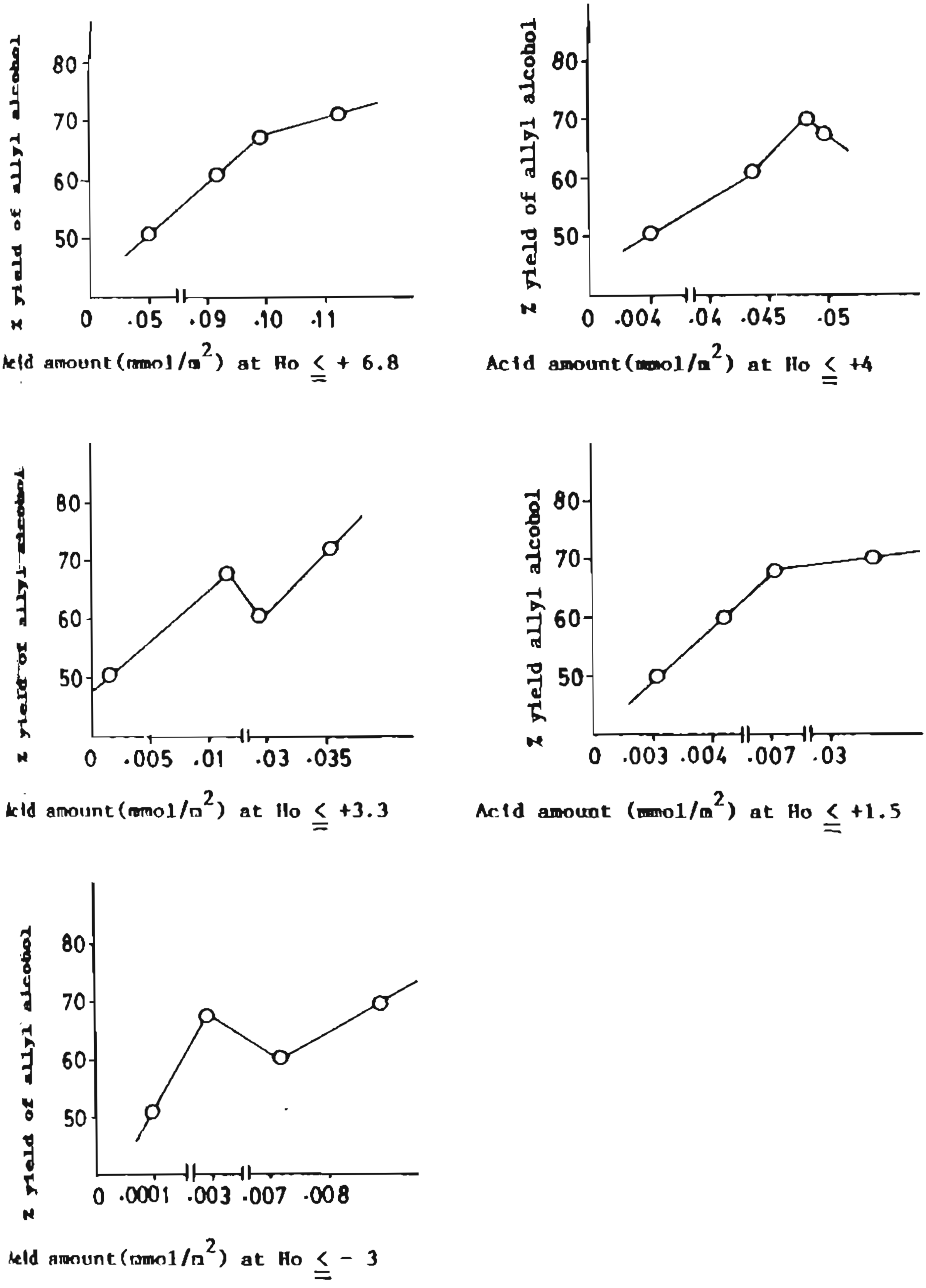


Fig.33. Variation in the percentage yield of Benzene-1-(1',5'-dimethyl -5'-hexenyl-4'-ol)-4 methyl with acid amount.

CHAPTER - IV

SURFACE CHARACTERISTICS AND CATALYTIC ACTIVITY OF BINARY OXIDE Al_2O_3-Y_2O_3 IN THE ISOMERIZATION OF (+) - LIMONENE OXIDE

4.1 Introduction

Properties of a catalyst largely depend on its surface properties like porosity, surface area, crystallinity, acidity, basicity as well as its composition. The above mentioned qualities like catalyst texture and stability can be modified by different preparation conditions. Since coprecipitation is the method of preparation used for the catalyst, the precipitated binary oxide will be having properties different from that of component oxides.

Binary oxide catalysts are widely used as catalysts and catalyst supports and their surface and catalytic properties have been described by a number of workers.[58,171-174] Al_2O_3 had been widely used as a catalyst and catalyst support. Investigators like Peri[175,176], Dabrowski[177], Knözinger, Ratnaswamy[178] and Ellis[179] made attempts to propose mechanisms for the activity of Al_2O_3. Fukuda and co-workers reported Y_2O_3 as a basic oxide, but less basic than alkaline earth oxide[63]. The introduction of varying amounts of Y_2O_3 in Al_2O_3 alter the properties of both Al_2O_3 and Y_2O_3.

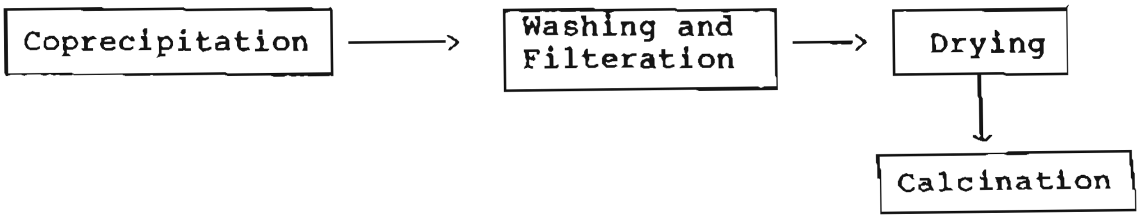
In previous chapters, 1:1 mixture of alumina-rare earth oxides like Al_2O_3-Y_2O_3, Al_2O_3-Sm_2O_3, Al_2O_3-Eu_2O_3, Al_2O_3-Nd_2O_3 and Al_2O_3-Pr_6O_{11} were made, characterised and their activity determined in the transformation of terpenyl oxiranes like α, β- pinene oxides, (+), (-) limonene oxides, 3-carene oxide and ar-curcumene oxide. It was observed that all the binary oxides except Al_2O_3-Y_2O_3 had similar acidic and basic properties with varying reactivities in the transformation of terpenyl oxiranes. Yttrium is always treated as part of the lanthanide group even though it is one period behind lanthanides in the periodic table. Properties of yttrium had been found to be similar since they are in the same group. The slightly different properties and activity of Al_2O_3-Y_2O_3(1:1) catalyst propelled the author to investigate the change in properties and reactivity with variation of Y_2O_3 in the composition of Al_2O_3-Y_2O_3 catalyst.

In the present chapter catalysts of Al_2O_3-Y_2O_3 having different compositions were prepared following the coprecipitation technique. Physico-chemical nature of catalysts were characterised and their activity determined in the transformation of (+)-limonene oxide.

4.2 Preparation and Physico Chemical Characterisation of Catalysts

4.2.1 Preparation of Catalysts

The various steps involved in the preparation can be outlined as below :



Scheme 1 : Steps involved in the preparation of binary oxide catalysts

Preparation of single oxides, Al_2O_3 and Y_2O_3 are given in section 2.2.6.1 and 2.2.6.2.

4.2.2 Preparation of Binary Oxides

The principles of various steps involved in the preparation are briefly outlined in section 2.2.1 to 2.2.5. Al_2O_3-Y_2O_3 catalysts in the compositions of 9:1, 7:3, 1:1, 3:7 and 1:9 are prepared.

4.2.2.1 Materials

$Al(NO_3)_3.9H_2O$ (A.R. grade supplied by E.Merck (India) Ltd), Y_2O_3 (99.9% pure supplied by Indian Rare

Earths Ltd, Alwaye), NH_4NO_3 (A.R. grade supplied by B.D.H), 25% NH_3 *solution (supplied by E. Merck (India) Ltd) and 50%* HNO_3.

Experimental

4.2.2.2 Preparation of Al_2O_3-Y_2O_3(9:1)

$Al(NO_3)_3.9H_2O$ (331.2 g) dissolved in 1000 ml water. 5 g of Y_2O_3 was dissolved in minimum amount of 1:1 HNO_3 and it was added to water solution containing $Al(NO_3)_3.NH_4NO_3$ (100 g) added to the mixed solution. The solutions were well mixed and 25% NH_3 added with stirring. The precipitated hydroxide was aged for 20 hr and washed with plenty of water. The precipitate was filtered through Whatman No.1 filter paper and dried at 130°C for 24 hr. The precipitate was calcined at 400°C for 5 hr.

4.2.2.3 Preparation of Al_2O_3-Y_2O_3 (7:3)

$Al(NO_3)_3.9H_2O$ (257.6 g) dissolved in 1000 ml water. 15 g of Y_2O_3 dissolved in minimum amount of 50% HNO_3 and mixed with aluminium nitrate solution. 100 g of NH_4NO_3 added to the mixture followed by 25% NH_3 solution with stirring. The precipitate was aged for 20 hr and washed with plenty of water. The precipitate was filtered through whatman No.1 filter paper and dried at 130°C for 24 hr and calcined at 400°C for 5 hr. Preparation of Al_2O_3-Y_2O_3 (1:1) is described in section 2.2.7. The same procedure is followed in making the catalyst.

4.2.2.4 Preparation of Al_2O_3-Y_2O_3 (3:7)

$Al(NO_3)_3.9H_2O$ (110.4 g) dissolved in 1000 ml water. 35 g of Y_2O_3 dissolved in minimum amount of 50% HNO_3 and both solutions were mixed together. 100 g of NH_4NO_3 added to that solution followed by 25% NH_3 solution. The solution was stirred well during NH_3 addition. The precipitate was kept in the solution for 20 hr and washed with plenty of water and filtered. The precipitate dried at 130°C for 24 hr and calcined at 400°C for 5 hr.

4.2.2.5 Preparation of Al_2O_3-Y_2O_3 (1:9)

$Al(NO_3)_3.9H_2O$ (36.8g) was dissolved in 1000 ml water. Y_2O_3 (45 g) was dissolved in minimum amount of 50% HNO_3 and mixed to the $Al(NO_3)_3$ solution. Then 100 gm of NH_4NO_3 added followed by 25% NH_3 solution with stirring. The precipitate was kept in solution for 20 hr and washed with water to remove impurities. It was then filtered and dried at 130°C for 24 hr and calcined in air at 400°C for 5 hr.

4.3 Chemical Analysis of Catalysts

Principle

Ytrrium present in these catalyst mixtures were precipitated as its oxalate by oxalic acid from its solution[138]. The oxalate was ignited to oxide and its weight determined. From the weight of oxide, weight of alumina in the mixture was estimated. The weight of each component in

Table 31

Chemical Estimation Values of Different Catalysts

Catalyst	Estimated value(w/w)
Al_2O_3-Y_2O_3(9:1)	11.5:1
Al_2O_3-Y_2O_3(7:3)	2.8:1
Al_2O_3-Y_2O_3(1:1)	1.05:1
Al_2O_3-Y_2O_3(3:7)	0.47:1
Al_2O_3-Y_2O_3(1:9)	0.12:1

Experimental

Procedure for the chemical estimation is given in *section 2.3.2. In each case the composition of catalyst is found to be close to the theoretical value.*

Surface Properties of Catalysts

4.4 Surface Area

Surface area of the catalyst was determined by BET method of N_2 adsorption at -196°C. The powder is cooled to -196°C and surface is incremently exposed to N_2 till the surface gets a unimolecular layer cover of adsorbent. Surface area of the solid was calculated by multiplying the number of molecules of N_2 gas required to form a unimolecular layer times the area covered by each molecule. The principle and procedure of the method is described in section 2.4.2 and 2.4.3. Table 32 gives the surface area values of different catalysts obtained by BET method.

Table 32

Specific Surface Area Values of Various Catalysts Obtained by BET Method.

Catalyst	Surface area m^2/g
Al_2O_3-Y_2O_3 (9:1)	144.9
Al_2O_3-Y_2O_3 (7:3)	126.7
Al_2O_3-Y_2O_3 (1:1)	101.8
Al_2O_3-Y_2O_3 (3:7)	23.62
Al_2O_3-Y_2O_3(1:9)	16.55

4.5 Pore Size Distribution

Mercury intrusion technique was used to determine the pore size distribution of catalysts. Autoscan 60 porosimeter was used for mercury intrusion. The principle and procedure are described in section 2.5.2 and 2.5.3. Pore surface areas obtained for different catalysts are given in Table 33 and pore size distribution curves of different catalysts are given in Figure 34.

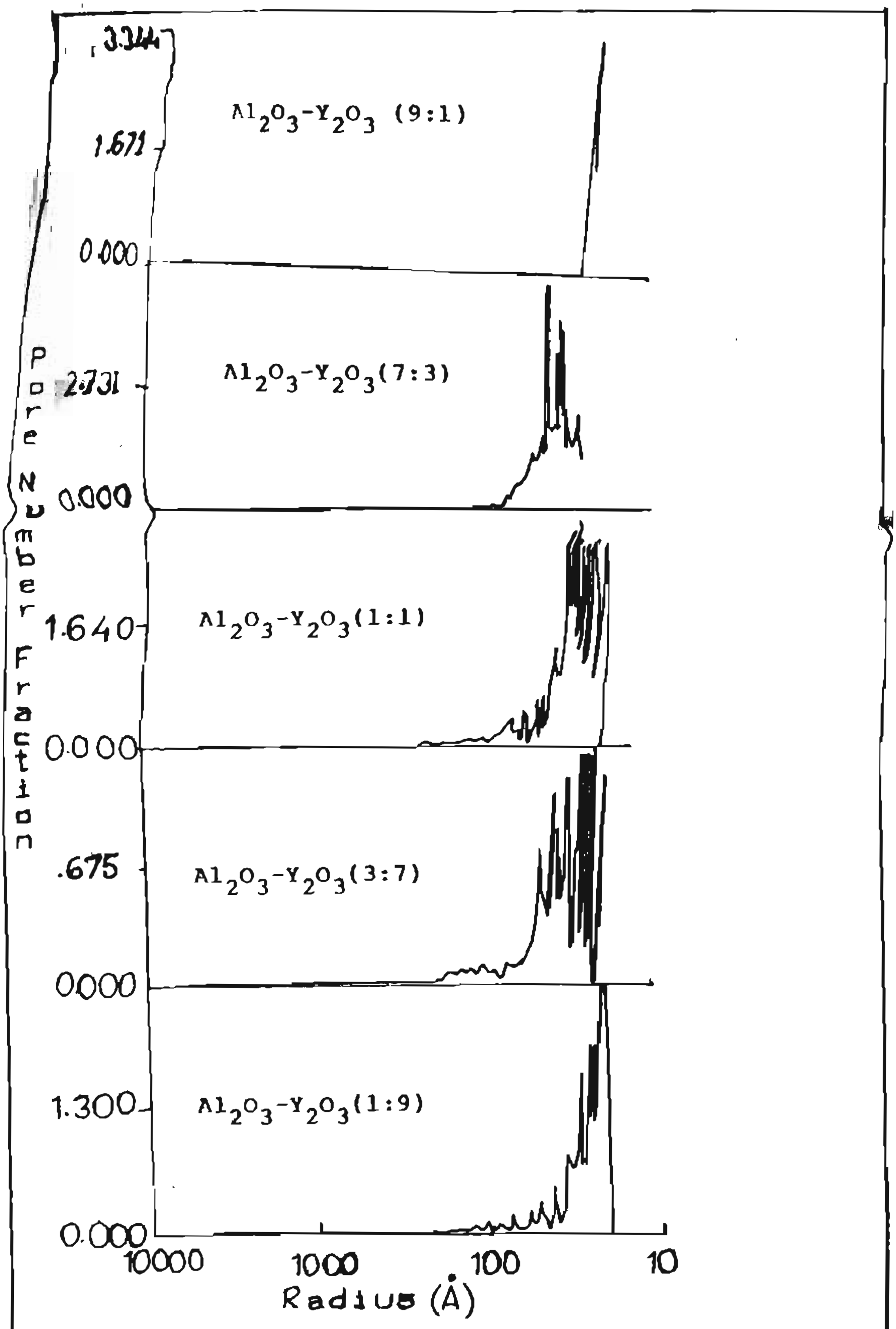


Fig. 34. Pore size distributions of Al_2O_3-Y_2O_3

Table 33

Pore Surface Area of Various Catalyst Mixtures

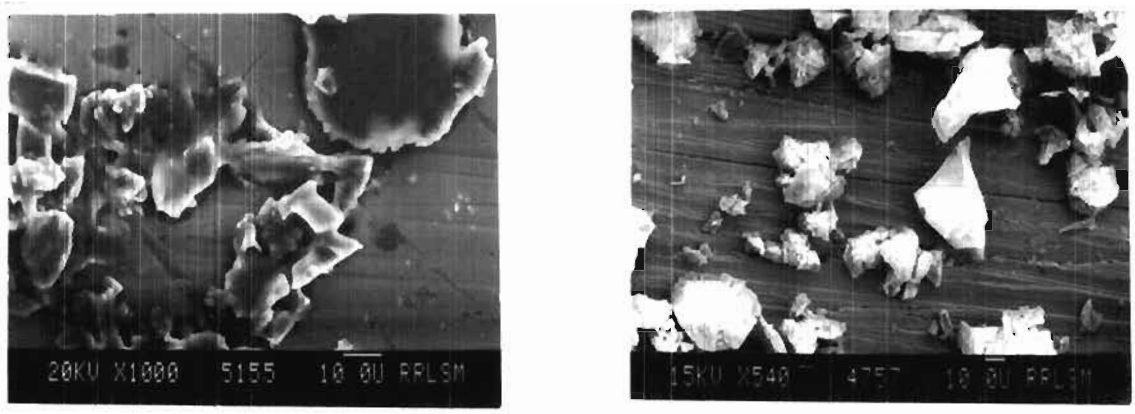
Catalyst	Pore surface area in m^2/g
Al_2O_3-Y_2O_3 (9:1)	64.77
Al_2O_3-Y_2O_3 (7:3)	56.48
Al_2O_3-Y_2O_3 (1:1)	30.64
Al_2O_3-Y_2O_3 (3:7)	23.89
Al_2O_3-Y_2O_3 (1:9)	11.79

4.6 Scanning Electron Microscopy

4.6.1 Principle

A stream of electrons generated from a heated tungston filament and accelerated by a potential upto 50 kV, are focussed by a series of electromagnetic lenses, into a fine probe so that when this strikes the object, it may have a dimeter of ~10 nm. The probe is caused to move over the surface of object in a zig-zig raster by two pairs of deflecting coils which carry current from a scan generator. The same current traverses the coils of a cathode ray tube, to produce on the screen an identical but a longer raster. The electron probe striking the specimen creates secondary

a. Al_2O_3 b. Al_2O_3-Y_2O_3(9:1)



c. Al_2O_3-Y_2O_3 (7:3) d. Al_2O_3-Y_2O_3(1:1)

e. Al_2O_3-Y_2O_3 (3:7) f. Al_2O_3-Y_2O_3(1:9)

Fig. 35. SEM of Different Al_2O_3-Y_2O_3 Compositions

electron micrographs of various catalysts are given in Fig.35.

4.7 X-ray Diffraction Studies

X-rays are electromagnetic waves of shorter wave length which incident on a parallel closely spaced planes of atoms within a crystal. The condition for reflection is the well known Bragg equation $n\lambda = 2d \sin\theta$. The instrument used in the present study was PW 1710 Phillips Holland which works in an emission current of 10 mA. Source in diffraction was CuKα radiation and sample scanned at an angle 20-60°. Figs. 36 and 37 give the XRD pattern of all catalysts. The principle and procedure of the method are given in section 2.6

4.8 Thermogravimetric analysis

The principle and procedure for this method are given in section 2.7

Samples are heated at a rate of 20°C/min., non-isothermally in air upto 850°C. The weight loss of the sample is measured as a function of temperature. The derivative curve (DTG) is obtained by the electronic differentiation of the TG signal. The instrument used was 951 Dupont thermal balance. Fig.38 gives the thermal analysis diagrams of catalyst samples.

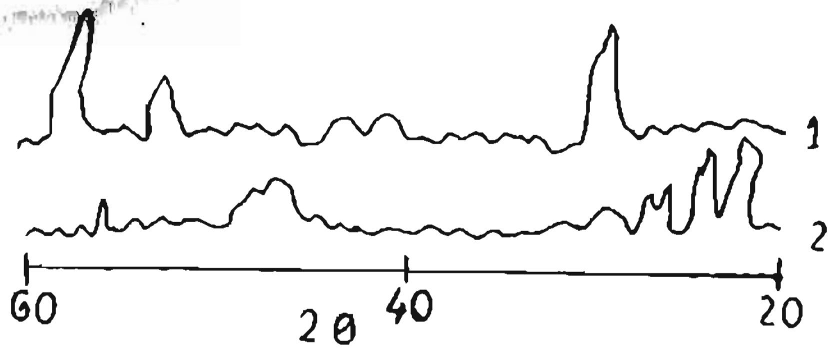


Fig. 36 XRD of Single Oxides

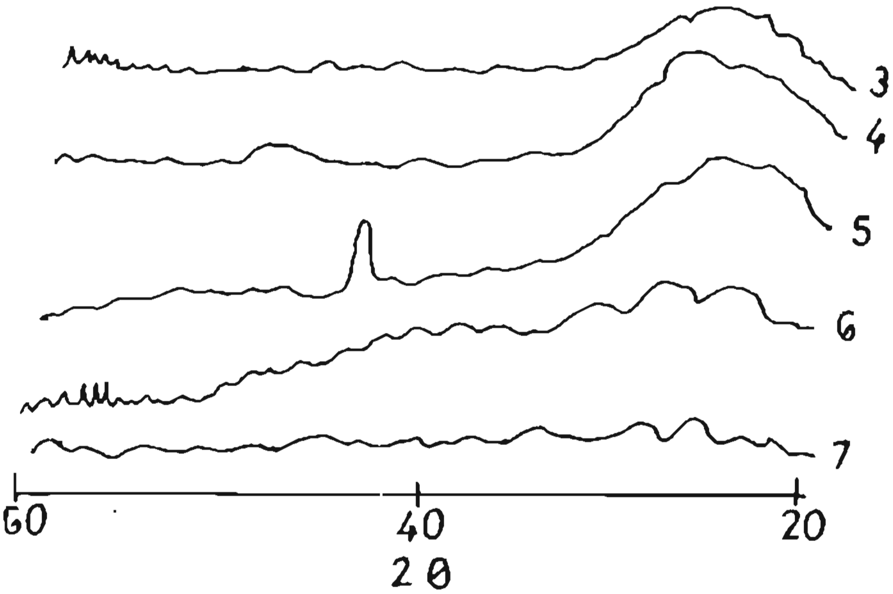


Fig. 37 XRD of Binary Oxides

1. Y_2O_3 2. Al_2O_3 3. Al_2O_3-Y_2O_3 (1:9)

4. Al_2O_3-Y_2O_3(3:7) 5. Al_2O_3-Y_2O_3(1:1)

6. Al_2O_3-Y_2O_3(7:3) 7. Al_2O_3-Y_2O_3(9:1)

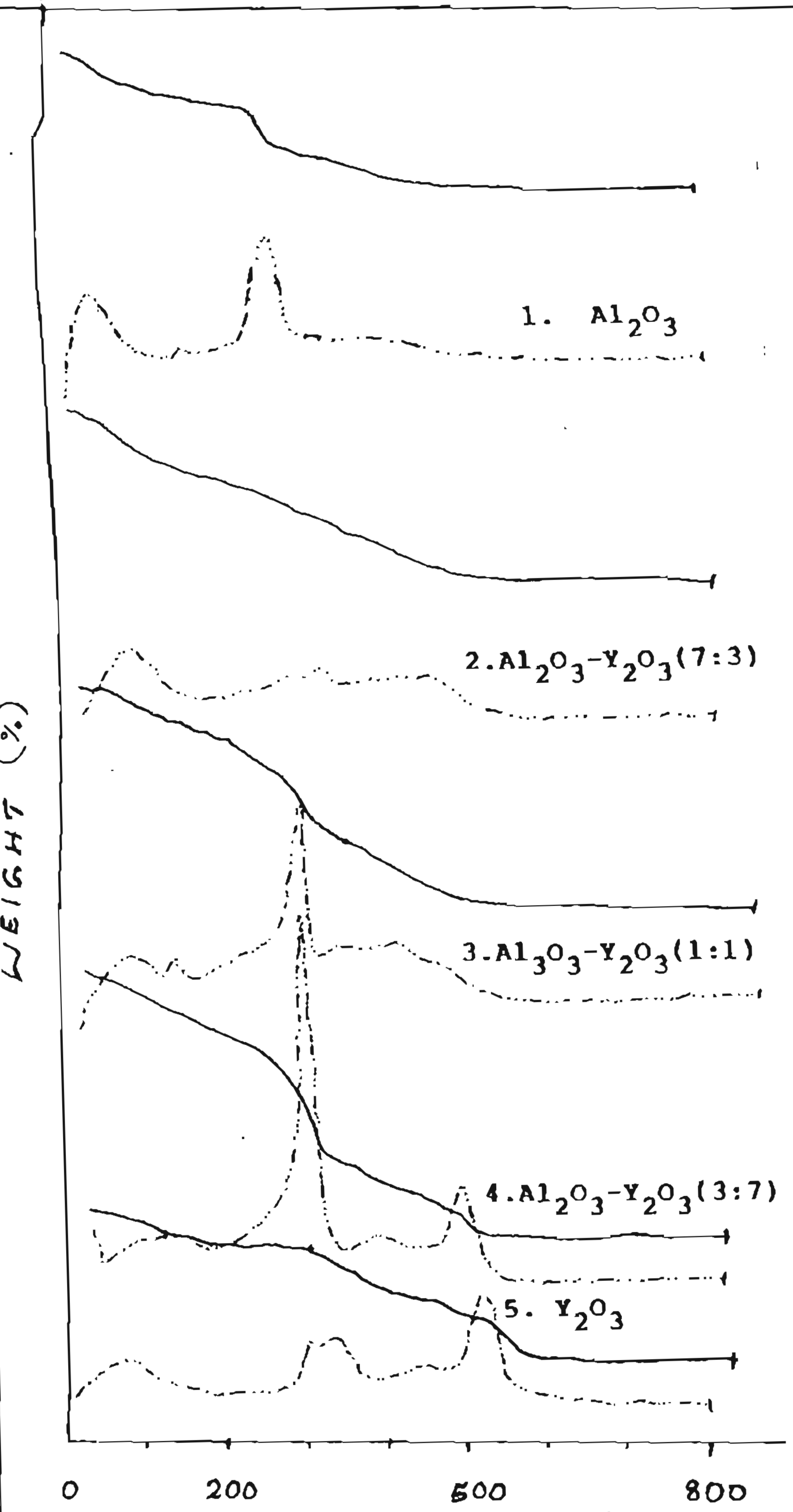


Fig. 38. TGA(-) and DTG (.-.) Diagram of Catalysts

4.9 Acidity and Basicity Measurements

Materials

Benzene (supplied by E. Merck (India) Ltd.), n-$BuNH_2$ supplied by S.D. Fine Chemicals. Indicators used in the present study are supplied by Aldrich Chemical Company Ltd. Purification of solvents are given in section 2.8.1. Table 9 gives the name of indicators used in the acidity determination.

4.9.1 Acid Strength Measurements

Various Hammett indicators are used for acid strength measurements. Procedure for acid strength determination is given in section 2.8.2.

4.9.2 Acidity of Catalyst Surface

Acidity of catalyst surface was estimated by titration with n-butyl amine using various Hammett indicators following Benesi's method[37].

4.9.3 Experimental

The procedure for determination of acidity of catalyst's surface is given in section 2.8.3. The acid strength and acid amount of different catalysts are given in Table 34 and 35 respectively.

Table 34

Acid Strength of Various Catalysts

Catalyst	Ho-range
Al_2O_3	-5.6 to -8.1
Y_2O_3	+1.5 to + 3.3
Al_2-Y_2O_3(9:1)	-5.6 to -8.1
Al_2O_3-Y_2O_3 (7:3)	-5.6 to -8.1
Al_2O_3-Y_2O_3(1:1)	-5.6 to -8.1
Al_2O_3-Y_2O_3 (3:7)	+1.5 to +3.3
Al_2O_3-Y_2O_3 (1:9)	+1.5 to +3.3

Table 35

Acid Amount of Various Catalysts in m mol/m^2

Catalyst	Acid amount in m mol/m^2 in the Ho range					
	+6.8	+4	+3.3	+1.5	-3	Total acidity
Al_2O_3-Y_2O_3(9:1)	0.0837	0.0242	0.0114	0.0031	0.0006	0.1232
Al_2O_3-Y_2O_3(7:3)	0.0631	0.0165	0.0063	0.0023	0.0001	0.0885
Al_2O_3-Y_2O_3(1:1)	0.0589	0.0044	0.0021	0.0030	0.0001	0.0687
Al_2O_3-Y_2O_3(3:7)	0.0846	0.0338	0.0067	-	-	0.1253
Al_2O_3-Y_2O_3(1:9)	0.0725	0.0241	0.0030	-	-	0.0996

4.9.4 Basicity Measurements

Materials

Cyclohexane (supplied by E. Merck (India) Ltd.), Benzene guaranteed reagent supplied by BDH and benzoic acid (95% pure) supplied by BDH. Indicators used in the present study and their color changes at different pKBH values are given in section 2.8.4. The indicator solutions are made by dissolving 1 g indicator sample in 1000 ml dry benzene.

Tables 36 and 37 give basic strengths and basicity values of different catalysts. The procedure for basicity determination are given in section 2.8.6.

Table 36

Basic Strengths of Various Catalysts

Catalyst	H_- value
Al_2O_3-Y_2O_3(9:1)	+15 to 18.4
Al_2O_3-Y_2O_3(7:3)	+15 to 18.4
Al_2O_3-Y_2O_3 (1;1)	+15 to 18.4
Al_2O_3-Y_2O_3(3:7)	-
Al_2O_3-Y_2O_3(1:1)	-
Al_2O_3	+15 to 18.4
Y_2O_3	-

Table 37

Basicity of Different Catalysts

	Basicity in meq/m^2	
Catalyst	+12.2	+15
Al_2O_3-Y_2O_3 (9:1)	0.26	0.16
Al_2O_3-Y_2O_3 (7:3)	0.022	0.04
Al_2O_3-Y_2O_3 (1:1)	0.024	0.045

4.10 MAS ^{27}Al NMR Studies

^{27}Al is 100% abundant with I = 5/2 and a chemical shift range around 450 ppm. The line width of the ^{27}Al resonance is a sensitive function of the symmetry of the nuclear environment. Useful chemical information can be obtained from the spectra provided quadrupolar coupling and chemical shift effect can be separated[180]. The principle and procedure for this method is described in section 2.10.1 and 2.10.2. Fig. 39 illustrates the MAS ^{27}Al NMR of Al_2O_3-Y_2O_3 (1:1) spun at 3.34 and 4.03 kHz.

4.11 Catalytic Reaction

The activity and selectivity of the catalysts were checked in the isomerization of (+) -limonene oxide (97%

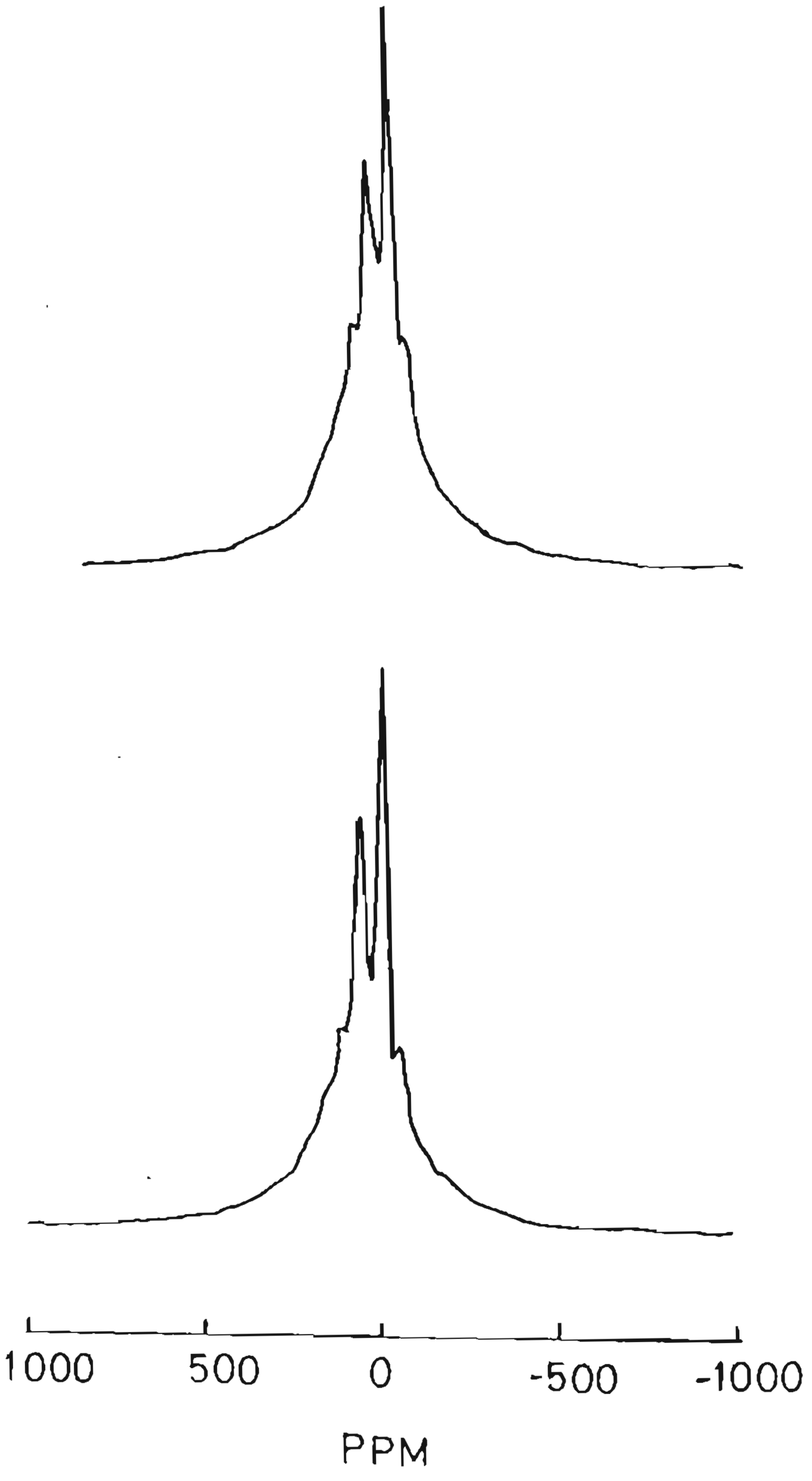


Fig. 39. MAS ^{27}Al NMR of Al_2O_3-Y_2O_3 Sample Spun at 3.34 and 4.03 kHz.

pure, *supplied* by Aldrich Chemical Company, U.S.A. and is a 1:1 mixture of cis and trans epoxide). Toluene and methylene chloride used were AR grade supplied by E. Merck (India) Ltd.

4.11.1 Experimental

(+)-Limonene oxide (200 g, 1.3 m mol), Al_2O_3-Y_2O_3 1 g and 5 ml solvent (toluene) were refluxed with stirring. Conversion rate of the reactant was monitored by TLC. After 8 hr the reaction was found to be very slow. Reaction mixture filtered to separate the catalyst, and the catalyst extracted with methylene chloride. All filtrates combined together and solvent removed. The same procedure was followed for all catalysts and reaction time was 8 hr.

4.11.2 Preparation of Authentic Samples

4.11.2.1 Preparation of Carveols

Materials

(+)-Limonene oxide, aluminium isopropoxide.

Experimental

Carveols were prepared by the same method given in section 3.5.3.2.

4.11.2.2 Preparation of (3-isopropenyl cyclopentyl) ketone

Materials

(+)-Limonene oxide, $ZnBr_2$, benzene

Experimental

Procedure same as given in section 3.5.3.1.

4.11.2.3 Preparation of Limonene Diol

Materials

(+)-Limonene oxide supplied by Aldrich Chemical Company, T.H.F. supplied by E. Merck (India) Ltd. and 1% H_2SO_4.

Experimental

Procedure same as given in section 3.5.3.3.

4.11.2.4 Preparation of 1-methyl-3-isopropenyl cyclopentyl -1-carboxaldehyde

Materials

(+)-Limonene oxide, $ZnBr_2$ and benzene.

Experimental

The method followed here is the procedure of Settine and co-workers[97]. (+)-Limonene oxide 3.9 g (0.026 mol) was taken in 100 ml dry benzene and refluxed. To the refluxing solution 1 g of $ZnBr_2$ added. Exothermic reaction occurred and external heating was stopped. The mixture refluxed for

2 hr and 200 ml water added. The benzene solution was separated and washed with water and dried over anhydrous sodium sulphate. Solvent removed and the crude material was fractionally distilled in vacuum. The first fraction collected at 76°C (10 mm of Hg) was aldehyde. Yield 1.1 g. Structure of aldehyde was confirmed from IR and NMR spectra. Purity of the product was found to be 87% by GLC analysis.

4.12 Identification of Products

Reaction products in the mixture were identified by GLC and GC-MS. Linalyl acetate was used as the internal standard in GLC analysis. GLC analysis was done on a 5840A Hewlett-Packard gas chromatograph. Column used OV17 (10%), 1.8 M length, 3.1 mm I.D., column temperature programme 80-200°C at the rate of 5°C/min. Injector was at 250°C and F.I.D. detector at 300°C. Carrier gas was helium at the rate of 20 ml/min.

GC-MS analysis was done on a Varion-3400 Incos 50 mass spectrometer. Column DB-5, length 30 M, I.D-2.5 nm, column temperature programme from 60-200°C at the rate of 5°C/min. Carrier gas used was helium. MS data given in each case is in the decreasing order of abundance.

Compound 4', 4, 56 and 5 were identified as trans-exo-carveol, cis-exo-carveol, trans-endo-carveol and cis-endo-carveol respectively by RRT and MS.

Compound 4' MS 119(100), 55, 67, 79, 91, 109, 119, 134, 105, 123.

Compound 4 MS 41(100), 81, 67, 55, 107, 93, 121, 136, 152.

Compound 56 MS 119(100), 134, 91, 92, 93, 109, 84.

Compound 5 MS 84(100), 134, 109, 41, 55, 119, 83, 91.

Compound 8 was identified as limonene diol by its RRT and MS. 43(100), 71, 67, 55, 82, 102, 88, 137, 152, 119, 101.

Compound 72 was identified as methyl-3-isopropenyl cyclopentyl ketone by comparing its RRT with standard and MS.

41(100), 55, 109, 84, 91, 69, 77, 119, 105, 134, 123, 152.

Compound 36 was identified as carvone by its RRT with an authentic sample and MS.

82(100), 110, 95, 39, 41, 54, 137, 152.

Compound 33 was identiied as 1-methyl-3-isopropenyl cyclopentyl carbaldehyde by its RRT with an authentic sample.

4.13 Results and Discussion

Varying compositions of Al_2O_3-Y_2O_3 were prepared by coprecipitation from their nitrate solution using 25% NH_3 as the precipitant. All binary oxides were prepared under the same condition. The final pH of the solution was 10.

Chemical estimation of the catalysts show that all the precipitated mixture are having composition close to theoretical value.

Surface Properties

4.13.1 Surface Area

The surface area of all binary oxide catalysts heated at 400°C and that of single oxides like Al_2O_3 and Y_2O_3 are presented in Table 32. The highest value of 156.1 m^2/g has been obtained in the case of Al_2O_3. These values start decreasing as the Y_2O_3 content increases. As can be seen in the case of thermal decomposition of yttrium hydroxide influence the decomposition of hydrous aluminium oxide such that the decomposition temperature has been brought down and surface area values obtained for these systems ideally support this observation. Since all the hydroxides were decomposed at 400°C over a period of 5 hr, the extent of decomposition occured in different mixtures would have been different. Some retaining residual OH groups still intact since the available reaction site depend on the available hydroxide and is also dependent on the effective surface area and microporosity and it can be assumed that alumina can definitely be most reactive. This can be made clear by specifically comparing the thermogravimetric curve of Al_2O_3 and Al_2O_3-Y_2O_3 (3:7) where the surface area are 156.1 m^2/g and 23 m^2/g respectively.

4.13.2 Pore Size Distribution

Fig. 34 present the pore number fraction versus radius for various oxide samples prepared for the present study. For Al_2O_3-Y_2O_3(9:1) there is a narrow distribution around 20Å and pore surface area 64.7 m^2/g. The narrowest distribution of pores is seen in the case of Al_2O_3-Y_2O_3 (9:1) which has also the lowest range of pore radius among the mixtures. This is indicative of the advantages with respect to specific surface area, decomposition pattern and reactivity compared to other compounds. In the case of Al_2O_3-Y_2O_3 (7:3) the distribution ranged from 20 to 150 Å with a pore surface area 56.4 m^2/g. For Al_2O_3-Y_2O_3 (1:1) there is a wide distribution pattern from 20 to 1000Å with a pore surface area 30.6 m^2/g. In the case of Al_2O_3-Y_2O_3 (3:7) the pore size varied from 20 to 250 Å with a pore surface area 23.89 m^2/g. For Al_2O_3-Y_2O_3 (1:9) the pore sizes still have smaller range from 20 to 200Å with a small pore surface are 11.79 m^2/g. As the yttrium content increases the pore size distributes over wider ranges. There is a general wide distribution tendency of pore size variation upto 1:1 composition with increase in yttrium content. The tendency is reversed although the best conditions for narrow distribution are seen in the 9:1 composition. There are large differences in the distribution patterns of different samples. Table 33 gives the pore surface areas of all catalyst compositions.

4.13.3 X-ray Difraction Studies

The x-ray diffraction patterns of all catalysts are shown in Figs. 36 and 37. Pure aluminium hydroxide calcined at 400°C shows highly amorphous nature probably because the decomposition is not complete and also because of residual microporosities. On *the other hand the hydrated yttrium oxide is purely crystalline* precipitate when heated at 400°C it has well defined pattern. As the yttrium content increases there is a partial crystallinity introduced in to the mixture on heating at 400°C which is supported by the thermogravimetric data. However all mixtures still retain the fineness possibly particle coarsening require still higher temperature. There is no visible indication possible from the XRD data excepting the fact that partial crystallinity introduced due to an optimum composition structure shown in Fig. 37 (9:1) could be the most ideal among the various compositions investigated. This is especially true because on the one hand pure $Al(OH)_3$ calcined at 400°C has a pattern very different from that of yttrium hydroxide at same temperature.

4.13.4 Microstructure

Fig. 35 present the morphological features of the partially dehydrated coprecipitates of Al_2O_3 and aluminium oxide-yttrium oxide coprecipitates. Pure $Al(OH)_3$ prepared in the present investigation has highly agglomerated solid morphology appearing as a partially decomposed gel. From the surface area data it is found that this hydroxide should have microporosites well distributed within the gel network due to the partial and slow evolution of the hydroxyls during calcination. This possibly is the reason for increased activity. Further it is observed from the XRD data that the partly calcined aluminium hydroxide is extremely fine and amorphous. On the other hand the morphological feature of (9:1) Al_2O_3-Y_2O_3 mixture is highly porous possibly having more of open pores due to the shifting of thermogravimetric peaks to lower temperature. There is only marginal difference in surface area from Al_2O_3 to Al_2O_3-Y_2O_3 (9:1). Al_2O_3 has got surface area 156.1 m^2/g while 9:1 mixture has a surface area of 144.4 m^2/g. Yttrium hydroxide in minor quantities probably influence the decomposition of the mixture such that the yttrium hydroxide decomposes preferntially leaving channels for the decomposition of aluminium hydroxide. This is made clear from the pore size distribution data where very narrow distribution is seen around 20A.

As the Y_2O_3 content increases the morphological features of calcined powder drastically changes as seen in Fig. 35. The surface area of this mixture is much lower compared to earlier. Samples for Al_2O_3-Y_2O_3 (7:3) surface area being 126.7 m^2/g and 101.8 m^2/g for Al_2O_3-Y_2O_3 (1:1). The pore size also distributes over a range possibly the decomposition of yttrium hydroxide and

$Al(OH)_3$ overlaps and hence the advantage of facilitating easy decomposition from the aluminium hydroxide phase is lost at this composition. This is seen from the data supported by XRD where a partial crystalline phase different from the pattern for pure $Al(OH)_3$ is observed as in Fig.36.

As the yttrium hydroxide content increases still the morphological feature of the partially calcined powder remain nearly the same indicating there could be an optimum aluminium oxide - yttrium oxide ratio for obtaining the right properties (Fig. 35). As evident from Table 32 the surface area of the catalyst decreases which is inexplicable from these observations.

4.13.5 Thermogravimetric Analysis

The thermogravimetric curve of hydrated aluminium oxide (Fig.38) shows initial loss of about 3% followed by a gradual decomposition to the basic oxide over a temperaure range of 850°C. There is a drop of about 18% weight around 300°C which is followed by a gradual reduction indicating the major phase being $Al(OH)_3$. On the other hand the thermogravimetric diagram for hydrated yttrium oxide shows a multiple decomposition pattern with a loss of about 13% in the first step around 300°C followed by about 16% above 500°C.

In the case of mixture of hydrated aluminium and yttrium oxides there is a common decomposition peak around 300°C accompanied by a loss of 28% which account for the joint losses from both hydroxides. However, due to the influence of the hydrated yttrium oxide the drastic reduction around 550°C has been smoothened out in the mixture. Thus, complete decomposition is made possible at a lower range. It is interesting to mention that the decomposition is more or less complete at around 500°C and nearly 60% remains undecomposed at 400°C.

4.13.5.1 Effect of Composition on the Decomposition of Oxides

In comparison of the thermal decomposition pattern of hydrated aluminium oxide, Al_2O_3-Y_2O_3 (1:1) and Al_2O_3-Y_2O_3(3:7), the following points are observed (Fig.38). As explained earlier while the major decomposition occurring at around 300°C is additive in nature ie. with increase of hydrated Y_2O_3, the extent of decomposition is 17%, 28% and 62% respectively for Al_2O_3, Al_2O_3-Y_2O_3(1:1) and Al_2O_3-Y_2O_3 (3:7). The final decomposition peak which is less predominent in the case of pure Al_2O_3 is distinctly getting clearer as the Y_2O_3 content increases with decomposition peak slightly less than 500°C for 3:7 mixture. It is concluded that Fig. 38 (3:7) that as a result of decrease in decomposition temperature with increase in Y_2O_3, the effective OH group remaining in the hydrated oxides is decreasing.

4.13.6 Acidic and Basic Properties

The total acidity in m mol/m^2 of various catalysts are given in Fig. 40. Total acidity increased with Al_2O_3 content in the catalyst. Acidity decreased from 0.1232 m mol/m^2 to 0.0687 m mol/m^2 when composition changed from Al_2O_3-Y_2O_3 (9:1) to Al_2O_3-Y_2O_3 (1:1). Total acidity increased to 0.1253 m mol/m^2 when Y_2O_3 content in the catalyst changed to 3:7. Catalyst samples which have higher amount of Y_2O_3 does not show any acidic sites of higher strength (Ho $\leq$ +1.5 and -3).

In Fig.41 acidic amount in m mol/m^2 of various catalysts are plotted against percentage of Y_2O_3. Among the different compositions of catalysts Al_2O_3-Y_2O_3 (9:1), (7:3) and (1:1) Al_2O_3-Y_2O_3 (9:1) showed more acid amount at various acid strengths. At Ho $\leq$ +6.8 an acid amount of 0.0837 m mol/m^2 was observed over Al_2O_3-Y_2O_3 (9:1) and it decreased to 0.0589 m mol/m^2 for Al_2O_3-Y_2O_3 (1:1).

For catalysts Al_2O_3-Y_2O_3(3:7), acid amount (Ho $\leq$ +6.8) increased to 0.0846 m mol/m^2 and the value decreased to 0.0725 m mol/m^2 for Al_2O_3-Y_2O_3 (1:9). The same trend can be observed for acid strengths at Ho $\leq$ +4 and

+3.3. *At acid amount +1.5,* Al_2O_3-Y_2O_3 (9:1) produced 0.003 m mol/m^2 and the value showed little variation for Al_2O_3-Y_2O_3 (1:1). At highest acid strength of Ho $\leqq$ -3 Al_2O_3-Y_2O_3 (9:1) produced 0.0006 m mol/m^2 and the value decreased to 0.0001 m mol/m^2 for Al_2O_3-Y_2O_3 (7:3).

From Table 37 it is clear that the catalyst with highest alumina content showed highest basicity. A decrease in basicity is observed from Al_2O_3-Y_2O_3 (9:1) to Al_2O_3-Y_2O_3 (7:3). Al_2O_3-Y_2O_3 (7:3) produced basicity of 0.022 meq/m^2 at H_-+12.2 and 0.04 meq/m^2 at H_-15.0 respectively. When composition changed to 1:1 mixture, Al_2O_3-Y_2O_3 had a basicity value of 0.024 meq/m^2 at H_-+12.2 and 0.045 meq/m^2 at H_-+15. Al_2O_3-Y_2O_3 (3:7), Al_2O_3-Y_2O_3(1:9) and Y_2O_3 showed no basicity values.

Al_2O_3 showed acid amounts of 0.1787, 0.1149, 0.1245 and 0.0191 m mol/m^2 at Ho $\leqq$ +6.8, +4, +3.3 and +1.5 respectively but no acid sites at Ho $\leqq$ -3 was observed. Al_2O_3 produced least basicity values of 0.051 meq/m^2 at H_-12.2 and 0.0766 meq/m^2 at H- 15. Y_2O_3 produced no basic color with indicators, but produced an acidity of 1.5 m mol/g at Ho $\leqq$+6.8, 5.6 m mol/g (Ho $\leqq$ +4) and 1.4 m mol/g at Ho $\leqq$ +3.3. No acidic sites were observed at Ho $\leqq$ +1.5 and -3 on the surface of Y_2O_3. Among the five different compositions of Al_2O_3-Y_2O_3 used in the study

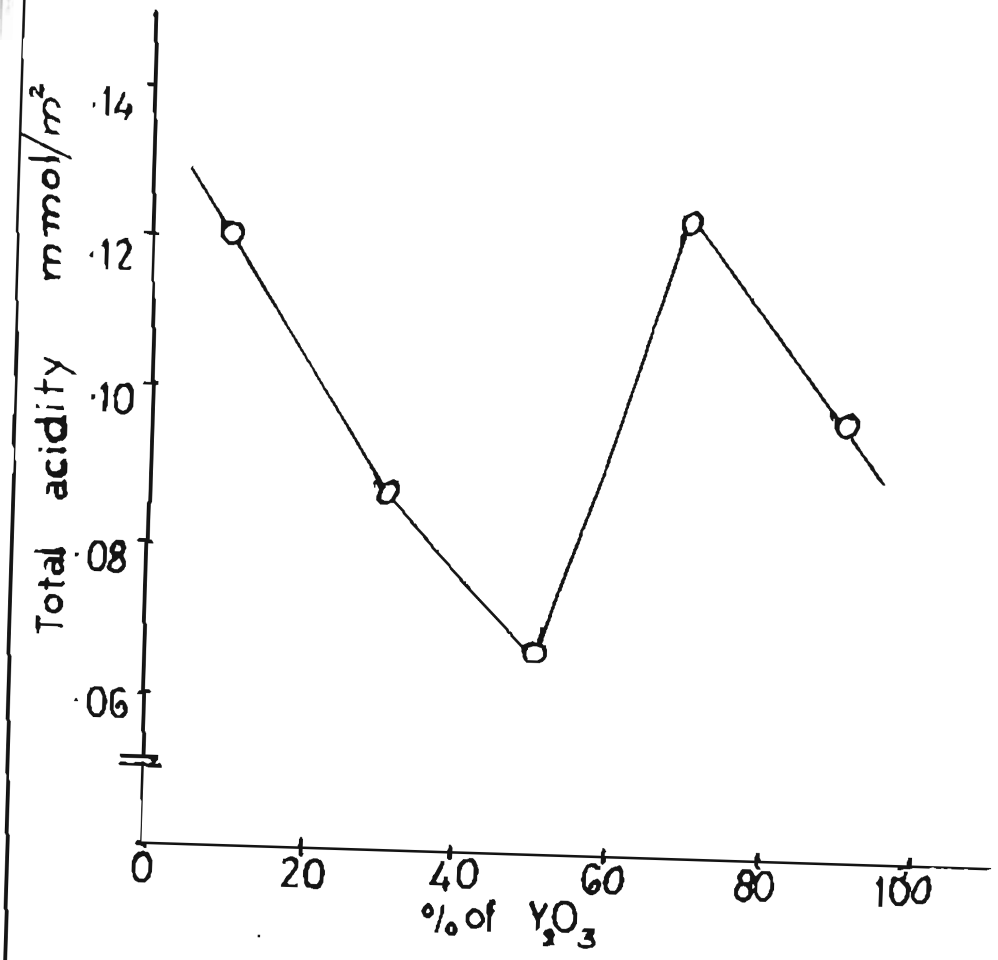


Fig.40 Total acidity variation with % of Y_2O_3

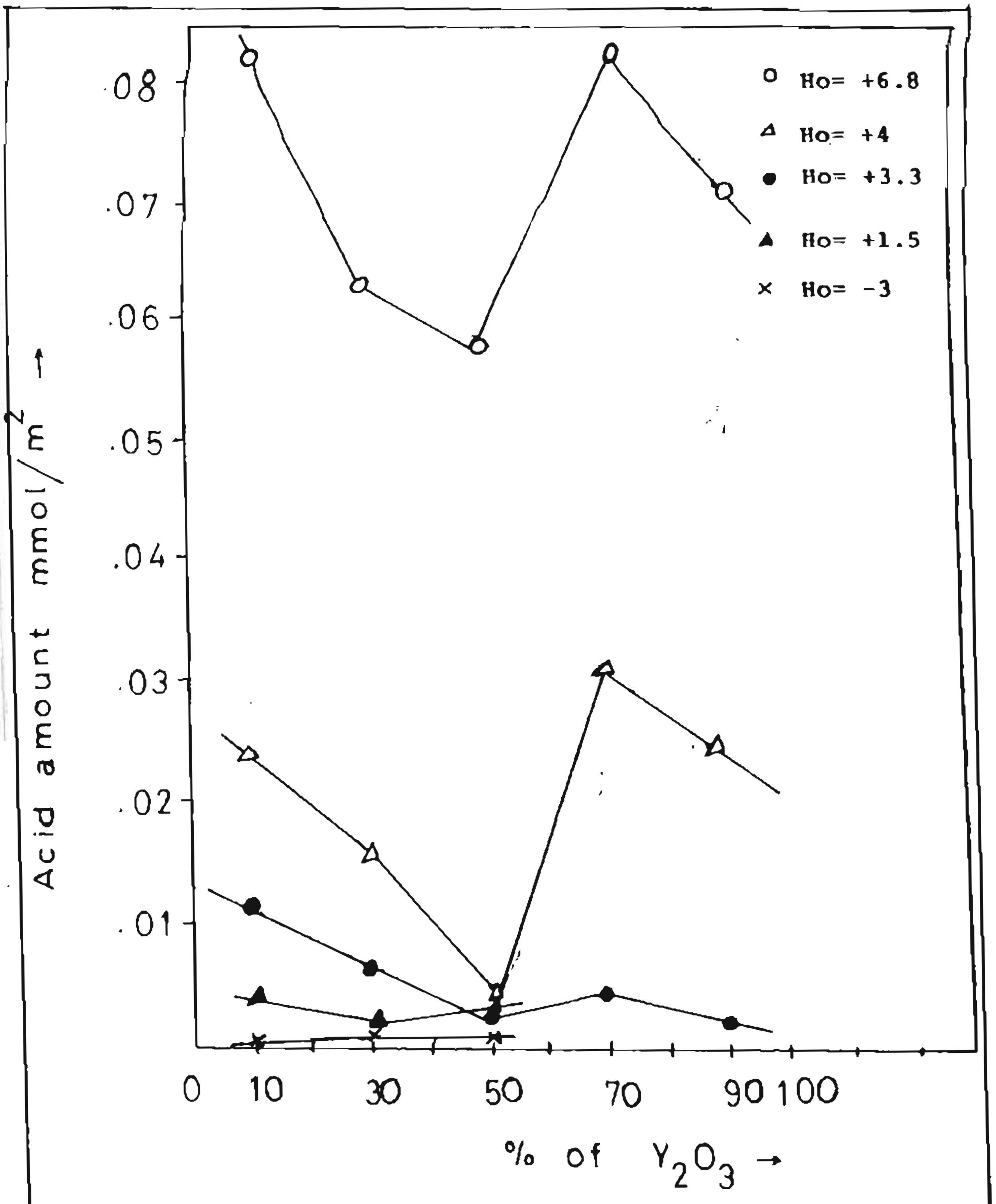


Fig. 41 Acid amount variation with % of Y_2O_3

Al_2O_3-Y_2O_3 (9:1), Al_2O_3-Y_2O_3 (7:3) and Al_2O_3-Y_2O_3 (1:1) showed acidic as well as basic sites.

4.13.7 Effect of Co-ordination on the Properties Al_2O_3-Y_2O_3

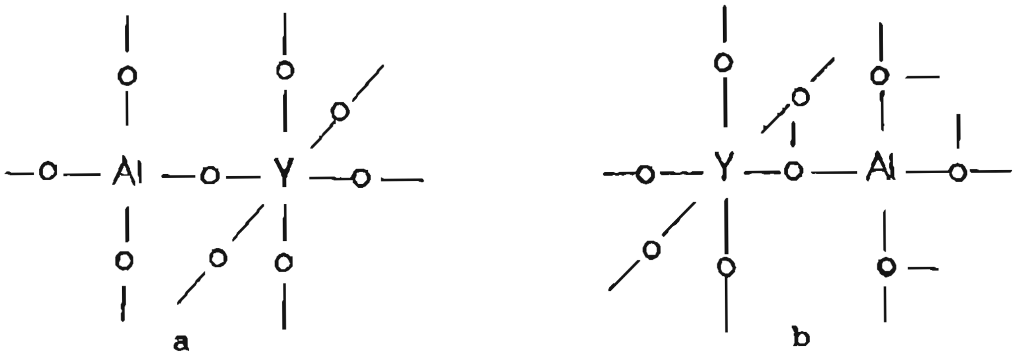
The MAS ^{27}Al NMR spectra of Al_2O_3-Y_2O_3 (1:1) is given in Fig. 39. Signals in the range of 7 ppm and 66 ppm showed octahedral as well as tetrahedral coordination of aluminium atoms in the mixed oxide. In the present study sample spun at 3.34 kHz and 4.03 kHz.

Tanabe's hypothesis[70] for the generation of surface acidity of binary oxides can be applied here also. From Fig. 39 it is beyond doubt that some Al atoms are in tetrahedral coordination while some are in octahedral coordination in the mixed oxides. In the binary oxide where Al_2O_3 being the major oxide (a), the three positive charges of yttrium are distributed to six bonds, while two negative charges of oxygen are distributed to two bonds.

The difference in charge for one bond is 3/6 - 2/2 and for all the bonds the valence unit of -1/2x6 = -3 in excess. In this case, Bronsted acidity is assumed to appear because three protons are associated with three oxygen atoms for electrical neutrality.

In the second case (b) where Al_2O_3 is the minor oxide, three positive charges of Al are distributed to four

Fig. 42 Model Structure of Al_2O_3-Y_2O_3



bonds, while two negative charges of oxygen are distributed to three bonds. The difference in charge for one bond is 3/4-2/3 and for all the four bonds the valence unit of 1/12x4 = 1/3 in excess. In this case Lewis acidity is assumed to appear on the catalyst. By titrimetric method, among the various compositions, Al_2O_3-Y_2O_3(9:1) was found to be most acidic among various compositions.

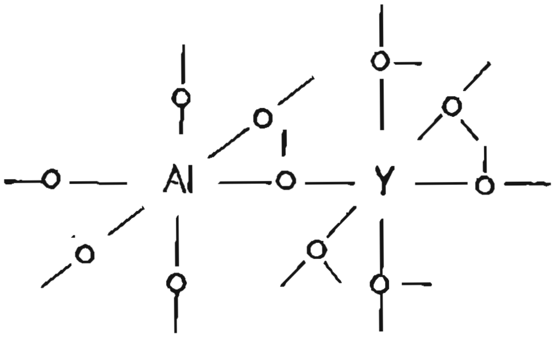


Fig.43 Model Structure of Al_2O_3-Y_2O_3 (octahedral)

In the octahedral coordination of aluminum, when Al_2O_3 is the major oxide the three positive charges of yttrium are distributed to six bonds while two negative charges of oxygen are distributed to three bonds. The difference in charge for one bond is 3/6-2/3 and for all the bonds the value is (3/6-2/3) 6 = -1 in excess. This shows Bronsted acidity only. When Y_2O_3 is in excess and Al_2O_3 the minor oxide, three positive charges of Al are distributed to six bonds, while two negative charges of oxygen are distributed to three bonds. The difference in charge for one bond is 3/6-2/3 and for all bonds the valence unit of (3/6-2/3) 6 = -1 in excess. In this case also Bronsted acidity appears on the catalyst surface.

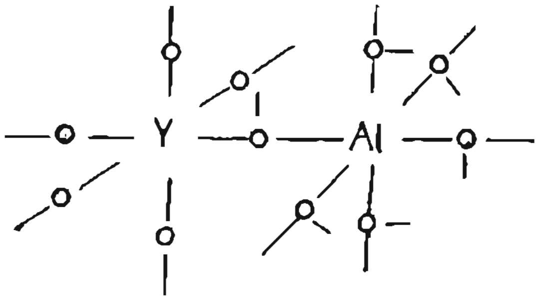
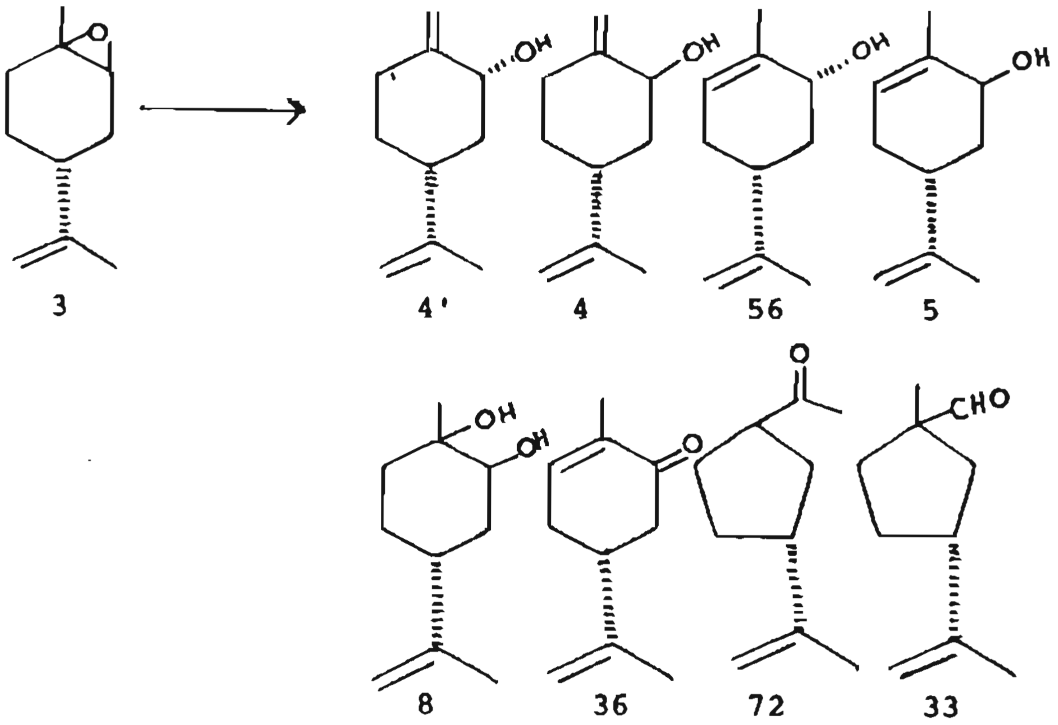


Fig.44 Model Structure of Al_2O_3-Y_2O_3

4.13.8 Catalytic Reactions

Catalytic activity of different compositions of Al_2O_3-Y_2O_3 was checked in the isomerization studies of (+) limonene oxide at 110°C. (+)-limonene oxide (3) isomerizes mainly to the following products, trans and cis exo-carveol (4',4) trans- and cis-endo-caraveol(56,5),8,(9) -p-menthene 1,2 diol (8), 1-methyl-3-isopropenyl cyclopentyl ketone (72), carvone (36) and 1-methyl 3-isopropenyl cyclopentyl carbaldehyde (33).



As the percentage of Y_2O_3 in the catalyst increases the catalytic activity decreases. Al_2O_3 and Al_2O_3-Y_2O_3 (9:1) showed 100% conversion to products. The selectivity of various catalysts are given in Table 38. Except Y_2O_3, all catalyst compositions showed a decrease in percentage conversion with increase in the percentage of Y_2O_3. Reactivity decreased from 75 to 30% as the composition changed from Al_2O_3-Y_2O_3 (7:3) to Al_2O_3-Y_2O_3 (1:9).

Table 38

Activity and Selectivity of Various Catalysts for Isomerization of (+)-Limonene Oxide

Catalyst	Conversion (%)	Products %							
		4'	4	72	56	8	5	36	33
Al_2O_3	100	-	14	8	8	65	12	2	12
Al_2O_3-Y_2O_3(9:1)	100	6	-	5	5	76	-	3	-
Al_2O_3-Y_2O_3(7:3)	75	18	17	-	8	55	-	10	-
Al_2O_3-Y_2O_3(1:1)	65	12	10	9	10	34	12	10	-
Al_2O_3-Y_2O_3(3:7)	55	11	22	-	8	15	-	-	-
Al_2O_3-Y_2O_3(1:9)	30	27	-	23	-	10	-	17	-
Y_2O_3	75	16	35	19	-	-	-	8	-

4.13.8.1 Trans-exo-carveol [2-Methylene cyclohexane-1-01-5 (1-methyl ethenyl] trans] (4')

The percentage yield increased from 6 to 18 from $Al_2O_3-Y_2O_3$ (9:1) to (7:3). $Al_2O_3-Y_2O_3$ (1:1) produced only 12% trans-exo-carveol and yield increased to 27% in the case of $Al_2O_3-Y_2O_3$ (1:9).

As evident from Fig. 45 the variation in the percentage yield of exo-carveol with acid amount is not regular. Percentage yield increased with increase in acid amount, again decreases and again increases. Hence a direct correlation cannot be obtained from the value.

4.13.8.2 Cis-exo-carveol [2-Methylene cyclohexane-1-01-5 (1-methyl ethenyl) cis] (4)

Pure Al_2O_3 produced 14% yield of cis-exo-carveol. The yield decreased from 17% to 10% as the composition of catalyst changed from $(Al_2O_3-Y_2O_3)$ 7:3 to 1:1. The percentage yield increased in 22 for $Al_2O_3-Y_2O_3$ (3:7). 35% yield of cis-exo-carveol was observed over Y_2O_3.

An attempt has been made to correlate the acid amount in m mol/m^2 to the yield of cis-exo-carveol at various acid amounts. As evident from Fig. 45 the percentage of cis-exo-carveol increased with acid amount over various

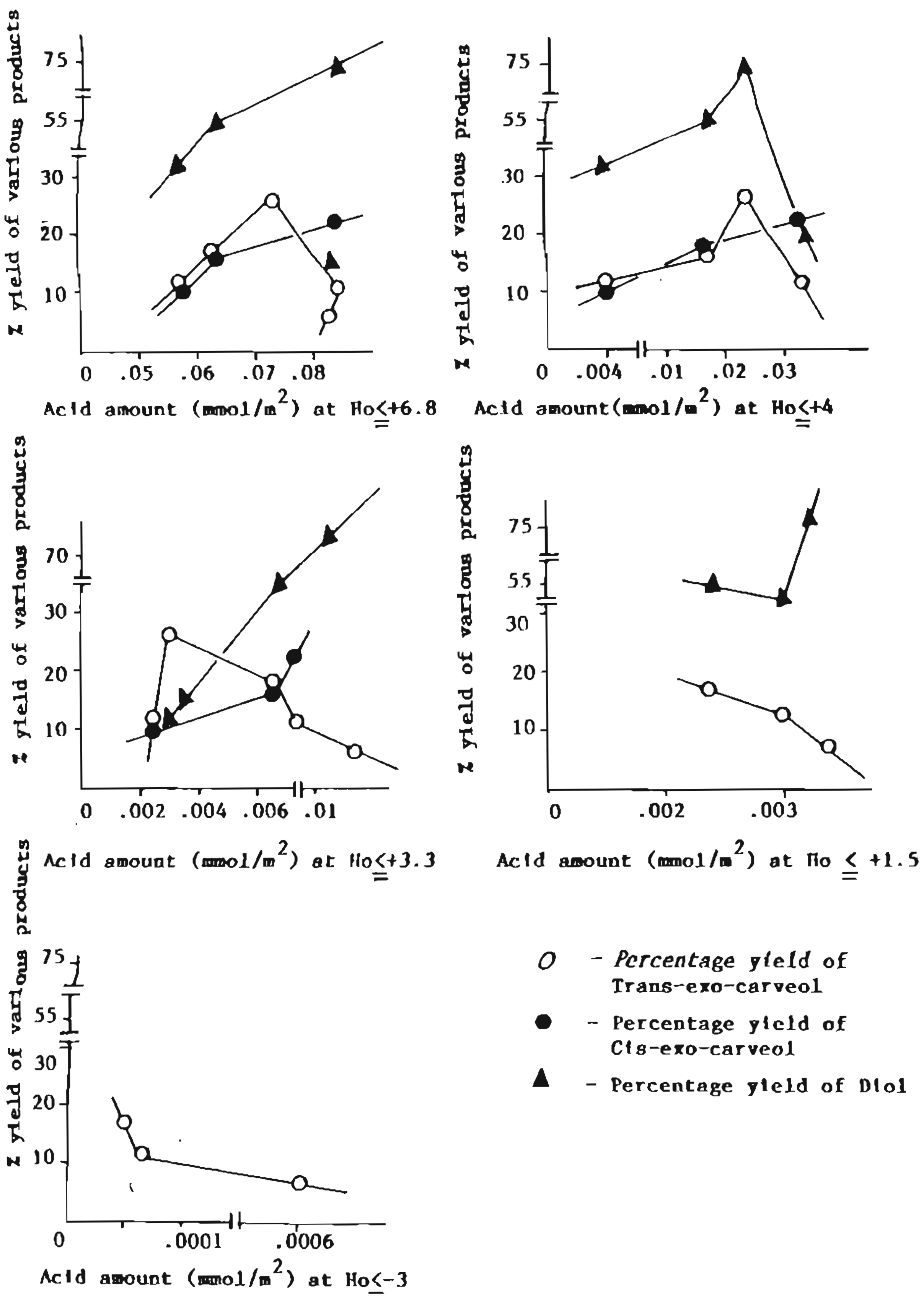


Fig.45 Percentage yield of various products with acid amount

catalysts Ho $\leq$ +6.8, and +3.3. At these Ho values (+6.8, +3.3), a correlation is obtained and over other acid strengths no correlation can be seen.

4.13.8.3 Trans-endo-carveol [2-Cyclohexene-1-01,2 methyl-5-(1-methyl ethenyl] trans] (56)

The yield of trans-endo-carveol is small over various catalysts. Al_2O_3-Y_2O_3 (1:1) alone produced 10% yield of trans-endo-carveol, over other catalysts yield varied from 5 to 8%.

4.13.8.4 Cis-endo-carveol (5)

Cis-endo-carveol was produced only over Al_2O_3 and Al_2O_3-Y_2O_3 (1:1) in 12% yield.

4.13.8.5 Carvone [2-cyclohexene-1-one, 2-methyl-5-[1-methyl ethenyl (36)]]

Carvone was produced in smaller amounts over all catalysts except Al_2O_3-Y_2O_3 (1:9). Al_2O_3-Y_2O_3 (1:9) yielded 17% carvone. Y_2O_3 produced 8% yield of carvone. Al_2O_3-Y_2O_3 (7:3) and Al_2O_3-Y_2O_3 (1:1) produced 10% of carvone.

4.13.8.6 8,(9)-p-menthene 1,2-diol (8)

Al_2O_3 produced 65% diol while Y_2O_3 yielded none. As the percentage of Y_2O_3 in the catalyst increased yield of diol decreased from 76 to 10%. Al_2O_3-Y_2O_3 (9:1) produced 76% diol and it changed to 34% over Al_2O_3-Y_2O_3 (1:1). The yield of diol decreased to 15% over Al_2O_3-Y_2O_3 (3:7) and to 10% over Al_2O_3-Y_2O_3 (1:9).

In Fig. 45 an attempt to correlate the acid amount in m mol/m^2 to yield of diol is illustrated. The percentage yield increased with acid amount in m mol/m^2 at some acid amounts like Ho $\leq$ +6.8, +4 and +3.3. At other Ho values no correlation can be observed from the data.

4.13.8.7 1-Methyl-3-isopropenyl cyclopentyl ketone (72)

The percentage yield of ketone was 8 on Al_3O_3 and 19 over Y_2O_3. Al_2O_3-Y_2O_3 (1:9) is the best catalyst for the formation of this ketone since it yielded 23%. Al_2O_3-Y_2O_3 (1:1) produced only 9% of ketone and the percentage yield decreased to 5 in the case of Al_2O_3-Y_2O_3 (9:1).

4.13.8.8 1-Methyl-3-isopropenyl cyclopentyl carbaldehyde (33)

Al_2O_3 alone produced 12% yield of this aldehyde.

4.14 Conclusion

Among the different compositions studied Al_2O_3-Y_2O_3 (9:1) showed maximum acidity, basicity and reactivity. The reason for the variation in properties of this catalyst can be attributed on the basis of thermogravimetric data. As the yttrium content increases the decomposition temperature of the mixed hydroxide is made to shift to lower ranges than pure $Al(OH)_3$ and pure $Y(OH)_3$. This fundamental difference in the catalyst nature leads to difference in properties like surface area, acidity, basicity, activity and selectivity.

CHAPTER - V

EFFECT OF PREPARATION AND PRETREATMENT CONDITIONS ON THE NATURE OF BINARY OXIDES OF Al_2O_3-Y_2O_3 AND ITS ACTIVITY FOR THE ISOMERIZATION OF (+) - LIMONENE OXIDE

5.1 Introduction

The nature of active sites on the surface of catalysts has been the subject of considerable investigation during the past 50 years. Particular attention has been given how the active sites on catalyst surface varied with preparation and pretreatment conditions. And also the overall performance of a catalyst is known to depend not only on the inherent catalytic activity of the active phase but also on the texture of the solid. The degree of control of surface area and pore size is possible during preparation and also by the use of additives.[181-190]

Alumina, a widely used catalyst and support[191] can be prepared with a range of surface areas[141] and pore sizes.[136,137,141,192-197] This versatality is in part due to different phases that may be produced on calcination. The nature and crystal forms of intermediates formed in the preparation also play an important role.

In the previous chapter various compositions of alumina-yttria catalyst are made and activity is checked in the reactions of (+)-limonene oxide. In the present chapter alumina-yttria (1:1) catalyst was made under different preparation conditions by coprecipitation and the activities checked in the isomerization study of (+) - limonene oxide.

5.2 Preparation of Catalysts

5.2.1 Materials

$Al(NO_3)_3.9H_2O$, 25% NH_3 solution, NH_4NO_3 supplied by E. Merck (India) Ltd. Y_2O_3 supplied by Indian Rare Earths Ltd; and 50% HNO_3 solution.

Experimental

5.2.1.1 Preparation of Al_2O_3-Y_2O_3 (1:1) - A_1

The method of preparation of (1:1) catalyst is briefly outlined in section 2.2.7. The precipitated hydroxide was washed with plenty of water, filtered, dried at 130°C for 24 hr and calcined at 600°C for 5 hr.

5.2.1.2 Preparation of Al_2O_3-Y_2O_3 (1:1)-A_2

Procedure followed was same as given in section 2.2.7. The precipitated hydroxide was washed and dried at 130°C for 24 hr and calcined at 800°C for 5 hr.

5.2.1.3 Preparation of Al_2O_3-Y_2O_3 (1:1)-A_3

Preparation of hydroxide was same as that given in section 2.2.7. The initial pH of the solution was kept at 4 when precursor solutions are mixed. 25% NH_3 added to complete the precipitation till pH changes to 10. The hydroxide was washed with water, filtered on a whatman. No.1 filter paper dried at 130°C for 24 hr and calcined at 400°C for 5 hr.

5.2.1.4 Preparation of $Al_2O_3-Y_2O_3$ (1:1)-A_4

Preparation followed the same procedure as in section 5.2.1.3. Only difference is pH of the initial solution was kept at 6 when precursor solutions are mixed.

5.2.1.5 Preparation of $Al_2O_3-Y_2O_3$ (1:1)-A_5

Preparation procedure for the hydroxide was same as given in section 2.2.7. The precipitated hydroxide was aged for 3 days washed, filtered, dried at 130°C for 24 hr and calcined at 400°C for 5 hr.

5.2.1.6 Preparation of $Al_2O_3-Y_2O_3$ (1:1) -A_6

Preparation method of hydroxide was same as in section 2.2.7. The precipitated hydroxide was aged for 7 days in solution, washed, dried at 130°C for 24hr and calcined at 400°C for 5 hr.

5.2.1.7 Preparation of $Al_2O_3-Y_2O_3$ (1:1) - A_7

Preparation method of hydroxide was same in section 2.2.7. The hydroxide was aged for 14 days in solution, washed, dried at 130°C for 24 hr and calcined at 400°C for 5 hr.

5.2.1.8 Preparation of Al_2O_3-Y_2O_3 (1:1)-A_8-By Homogenous Precipitation Using Urea

$Al(NO_3)_3.9H_2O$ (184 g) was dissolved in 1000 ml water. 25 g of Y_2O_3 dissolved in minimum amount of 50% HNO_3 and both solutions were mixed together. The solution boiled, and 200 g of urea added to that. After few minutes a precipitate was formed which was again boiled for 5 more minutes and kept for 20 hr. It is then washed with excess water, filtered and dried at 130°C for 20hr and calcined at 400°C for 5 hr.

5.2.1.9 Preparation of Recycling Catalysts

Al_2O_3-Y_2O_3 (1:1) was prepared as in section 2.2.7. This catalyst was used for recycling. After each reaction catalyst was refluxed with CH_3OH and extracted and calcined at 400°C. This procedure repeated after each reaction and catalyst was used for 5 cycles.

Physico-Chemical Characterisation of Catalysts

5.3 Chemical Analysis of the Catalysts

The precedure for chemical analysis is given in section 2.3.2. Yttrium present in each of the catalyst sample was precipitated as its oxalate by oxalic acid. Oxalate was washed and filtered on a whatman No.40 filter paper and ignited to oxide in a previously weighed crucible.

From the weight of yttrium oxide, the weight of alumina in the catalyst sample was determined. Table 39 gives the chemical analysis values of various catalysts.

Table 39

Chemical Estimation Values of Various Catalysts

Catalyst	Chemical estimation value w/w
Al_2O_3-Y_2O_3(1:1)-A_1	1.143:1
Al_2O_3-Y_2O_3(1:1)-A_2	1.125:1
Al_2O_3-Y_2O_3(1:1)-A_3	1.02:1
Al_2O_3-Y_2O_3(1:1)-A_4	1.096:1
Al_2O_3-Y_2O_3(1:1)-A_5	1.081:1
Al_2O_3-Y_2O_3(1:1)-A_6	1.042:1
Al_2O_3-Y_2O_3(1:1)-A_7	1.022:1
Al_2O_3-Y_2O_3-A_8	1.125:1

5.4 Surface Area Analysis

Surface area of various catalysts were determined by BET method of N_2 adsorption at -196°C. The instrument used was Quantasorb. Jr. The principle and procedure of the method are briefly outlined in section 2.4.2 and 2.4.3.

Surface area value of various catalysts are given in Table 40.

Table 40

Specific Surface Area of Various Catalysts

Catalyst	Surface area in m^2/g
Al_2O_3-Y_2O_3(1:1)-A_1	24
Al_2O_3-Y_2O_3(1:1)-A_2	59.6
Al_2O_3-Y_2O_3(1:1)-A_3	55.5
Al_2O_3-Y_2O_3(1:1)-A_4	133.3
Al_2O_3-Y_2O_3(1:1)-A_5	55.7
Al_2O_3-Y_2O_3(1:1)-A_6	28.7
Al_2O_3-Y_2O_3(1:1)-A_7	45
Al_2O_3-Y_2O_3(1:1)-A_8	46.8

5.5 Scanning Electron Microscopy

Section 4.6 gives the principle and procedure of this method. Jeol SEM JSM 35C was used for scanning studies. A water solution of the material was dispersed with ultrasonic sound. A drop of the solution was placed on the brass stub and coated with gold and used for SEM analysis.

5.6 X-ray Diffraction Studies

The principle, instrumentation and procedure of the method are outlined in 2.6.1 and 2.6.2. In the present study, instrument used was PW 1710 Phillips Holland. Source of X-rays were CuKα radiation and samples scanned at 20-60°. Fig.47 gives the XRD patterns of Al_2O_3-Y_2O_3 (1:1) precipitated at initial pH 4, pH 6 and Al_2O_3-Y_2O_3 (1:1) calcined at 600 and 800°C.

5.7 Acidity and Basicity Measurements

5.7.1 Acidity Measurements

Materials

Benzene, n-BuNH_2 (supplied by S.D. Fine Chemicals). Various indicators listed in Table 9 are used for the study. Purification of various materials are given in section 2.8.1.

Experimental

The method of Benesi[37] for determination of acidity is described in section 2.8.3. The amount and acidity of various catalyst samples are given in Tables 41 to 44.

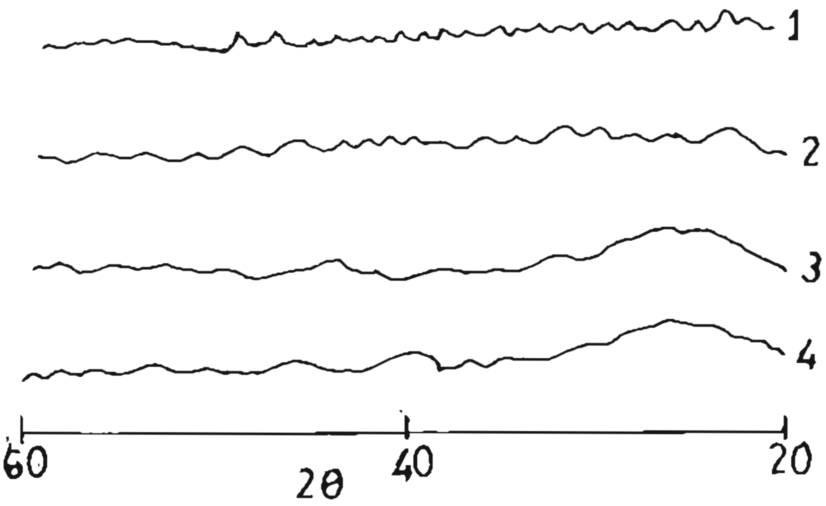


Fig. 47 XRD Spectra of Al_2O_3-Y_2O_3(1:1)

1. Catalyst prepared at pH^4
2. Catalyst made at pH^6
3. Calcined at 600°C
4. Calcined at 800°C

Table 41

Acid Strength of Various Catalysts

Catalyst	Acid strength(Ho)
Al_2O_3-Y_2O_3(1:1)-A_1	-5.6 to -8.1
Al_2O_3-Y_2O_3(1:1)-A_2	-5.6 to -8.1
Al_2O_3-Y_2O_3(1:1)-A_3	-5.6 to -8.1
Al_2O_3-Y_2O_3(1:1)-A_4	-5.6 to -8.1
Al_2O_3-Y_2O_3(1:1)-A_5	-5.6 to -8.1
Al_2O_3-Y_2O_3(1:1)-A_6	-5.6 to -8.1
Al_2O_3-Y_2O_3(1:1)-A_7	-5.6 to -8.1
Al_2O_3-Y_2O_3(1:1)-A_8	-3.0 to -5.6

5.7.2 Basicity Measurements

Materials

Cyclohexane, benzene, benzoic acid (all supplied by BDH). Indicators used in the present study are enlisted in Table 13 and procedure for basicity determination is briefly out lined in section 2.8.6.

Basicity was determined by the method of Yoneda[64b] et al. Table 45 gives the basicity values of different catalysts.

Table 42

Acid Amount of Various Catalysts at Different Ho Values

Catalyst	Acid amount at different acid strengths (Ho)					
	+6.8	+4	+3.3	+1.5	-3	Total acidity
Al_2O_3-Y_2O_3 (1:1)-A_1	0.3375	0.0333	0.0166	0.0083	0.0029	0.3986
Al_2O_3-Y_2O_3(1:1)-A_2	0.4084	0.045	0.0270	0.0220	0.0203	0.5227
Al_2O_3-Y_2O_3(1:1)-A_3	0.1801	0.3243	0.180	0.0090	0.0090	0.5404
Al_2O_3-Y_2O_3(1:1)-A_4	0.0375	0.2040	0.0090	0.0067	0.0037	0.2609
Al_2O_3-Y_2O_3(1:1)-A_5	0.0412	0.0987	0.0179	0.0170	0.0008	0.1756
Al_2O_3-Y_2O_3(1:1)-A_6	0.1742	0.5505	0.0348	0.0557	0.0034	0.8186
Al_2O_3-Y_2O_3(1:1)-A_7	0.1111	0.3511	0.0266	0.0622	0.0044	0.5554
Al_2O_3-Y_2O_3(1:1)-A_8	0.0096	0.0042	0.0032	0.0010	0.0064	0.0245

Table 43

Acid Strength of Recycled Catalysts

Catalysts	Acid strength
Catalyst II	-3 to -5.6
Catalyst III	-3 to -5.6
Catalyst IV	-3 to -5.6
Catalyst V	-3 to -5.6

Table 44

Acid Amount at Different Acid Strengths of Various Recycled Catalysts

Catalyst	Acid amount in m mol/g at various Ho values				
	+6.8	+4	+3.3	+1.5	-3
Catalyst II	0,2	0.15	0.2	0.15	0.3
Catalyst III	0.05	0.10	0.18	0.37	-
Catalyst IV	-	0.4	0.15	0.1 45	0.005
Catalyst V	-	0.2	0.15	0.15	

Table 45

Basicity Values of Different Catalysts in meq/m^2

Catalyst	Basicity values at different H_-values in meq/m^2			
	12.2	15	18.4	Total basicity
Al_2O_3-Y_2O_3(1:1)-A_1	4.916	0.0661	0.0166	4.983
Al_2O_3-Y_2O_3(1:1)-A_2	3.3898	0.5050	0.0033	3.9065
Al_2O_3-Y_2O_3(1:1)-A_3	1.0810	0.3783	0.0360	1.495
Al_2O_3-Y_2O_3(1:1)-A_4	0.5251	0.2850	0.0300	0.8401
Al_2O_3-Y_2O_3(1:1)-A_5	1.0771	3.554	0.1795	4.6449
Al_2O_3-Y_2O_3(1:1)-A_6	2.4390	7.4564	0.04878	9.9441
Al_2O_3-Y_2O_3(1:1)-A_7	1.333	6.200	0.0222	7.5552
Al_2O_3-Y_2O_3(1:1)-A_8	0.8119	0.2991	0.1709	1.2819

5.8 Catalytic Activity

The activity and selectivity of various catalysts were checked in the isomerization of (+)-limonene oxide.

5.8.1 Materials

(+)-Limonene oxide (1:1 mixture of cis and trans epoxide, 97% pure supplied by Aldrich Chemical Company U.S.A) solvents toluene, methylene chloride were guaranteed reagents.

5.8.2 Experimental

(+)-Limonene oxide (200 mg, 1.3 mmol). Al_2O_3-Y_2O_3 (1 g) and solvent (toluene, 7 ml) were refluxed with stirring. Reaction rate was monitored by TLC. After 8 hr, reaction was found to be slow. The reaction mixture filtered and catalyst extracted with methylene chloride. All filtrates combined together and solvent removed. The same procedure was followed for all catalysts including recycled one.

5.9 Preparation of Authentic Samples

5.9.1 Preparation of Carveols

Materials

(+)-Limonene oxide, Aluminium isopropoxide.

Experimental

The procedure for carveol preparation was given by Eschinasi[99] and described in section 3.5.3.2.

5.10.2 Preparation of (3-Isopropenyl cyclopentyl) Ketone

Materials

(+)-Limonene oxide, $ZnBr_2$ and dry benzene.

Experimental

The preparation followed the procedure of Settine[97] and described in section 3.5.3.1.

5.9.3. Preparation of Limonene Diol

Materials

(+)-Limonene oxide, THF solution, 1% H_2So_4.

Experimental

The preparation followed the procedure of Arbuzov[158] and given in section 3.5.3.3.

5.10 Identification of Products

Reaction products were identified by GLC and GC-MS analysis. GLC was done on a 5840 A Hewlett-Packard gas chromatograph. The column is used ov 17 (10%), 1.8M length; 3.1.m.m 1.D, column temperature, programme 80-200°C at the rate of 10°C/minute. Injector at 250°C and FID detector at 300°C. Carrier gas used was helium at the rate of 20 ml/minute. Linalyl acetate was the internal standard used.

GC-MS was done on a Varion 3400 Incos 50 mass spectrometer. column DB-5, length 30M, I.D 2.5 nm, column temperature programme from 60 to 200°C at the rate of 5°C/minute and carrier gas used was helium. MS values are given in the decreasing order of abundance.

Compound 32 was identified as p-cymene from its RRT with authentic sample and MS.

119(100), 91, 41, 77, 65, 51, 58, 103, 134, 74.

Compound 4' was identified as tran-exo-carveol by RRT and MS.

41(100), 55, 67, 79, 91, 109, 119, 134, 105, 123.

Compound 4 was identified as cis-exo-carveol by RRT and MS.

41(100), 81, 67, 55, 107, 93, 121, 136, 152.

Compound 56 was identified as trans-endocarveol by RRT and MS.

119(100), 134, 91, 92, 93, 109, 84.

Compound 5 was identified as cis-endo-carveol by RRT and MS.

84(100), 134, 109, 41, 55, 119, 83, 91.

Compound 36 was identified as carvone by its RRT with an authentic sample supplied by Fluka and MS.

82(100), 110, 95, 39, 41, 54, 137, 152.

Compound 8 was identified as 8,(9)-P-menthene 1,2-diol by its RRT with authentic sample and MS.

43(100),71,67,55,82,102,88,137,152,119,101.

Compound 72 was identified as methyl-3-isopropenyl cyclopentyl ketone by comparing its RRT with authentic sample and MS.

41(100), 55, 109, 84, 91, 69, 77, 119, 105, 134, 123, 152

5.11 Results and Discussion

Al_2O_3-Y_2O_3 (1:1) binary oxide catalysts were prepared by coprecipitation using 25% NH_3 solution and also by excess urea. Gravimetric estimation of the catalysts are given in Table 39. The composition of different oxides were close to theoretical values.

Surface Properties

5.11.1 Surface area

Table 40 give the surface area values of different catalysts by BET method. As evident from the thermogravimetric decomposition pattern in Fig.38, both Al_2O_3 and Y_2O_3 decomposed below 600°C and Y_2O_3 influence the decomposition pattern of Al_2O_3 such that the decomposition is 50% complete near 450°C. At 600°C, no phase separation for rare earth oxide is possible, but it is possible in the case of Al_2O_3. This is quite clear from XRD pattern of these catalysts. So a sharp increase in the surface areas of the catalyst from 24 m^2/g to 59.6 m^2/g was observed. When pH of the initial solution changed from 4 to 6 there is a tremendous increase in surface area from 55.5 m^2/g to 133.3 m^2/g. This may be due to partial gel formation with large microporosities at higher pH. An irregular change in surface area values observed with ageing. When alumina is precipitated its amorphous hydroxide is first formed which undergo phase change with ageing. Same phenomena happens when coprecipitate is formed. After ageing for a few days the precipitate will be considered to be a mixture of amorphous hydroxide along with various crystalline phases, the properties of each species present in the precipitate vary with ageing time. Hence the irregular variation in surface area can be accounted.

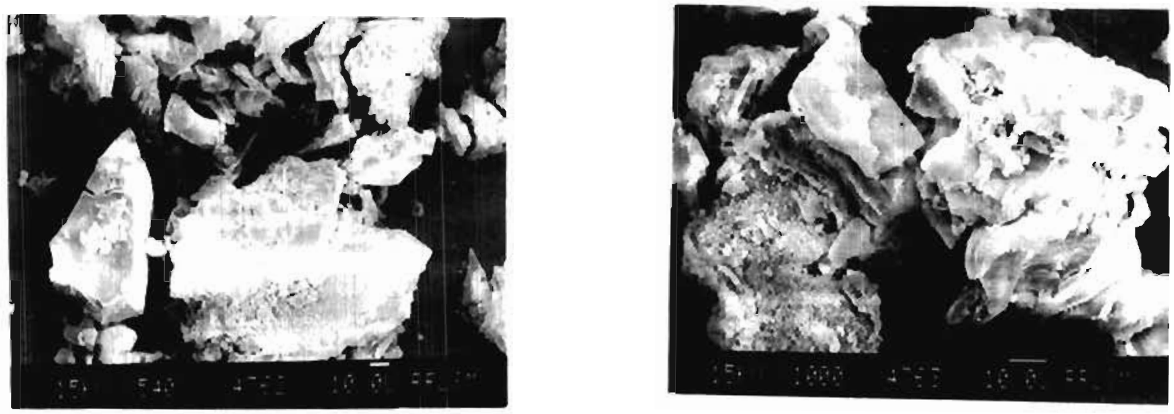
When urea is used as the precipitating agent, fine precipitate of hydroxide is formed with small particle size, but on boiling the smaller particles agglomerates to higher particles and hence surface area will be low as evident from Table 40.

5.11.2 X-ray Diffraction Studies

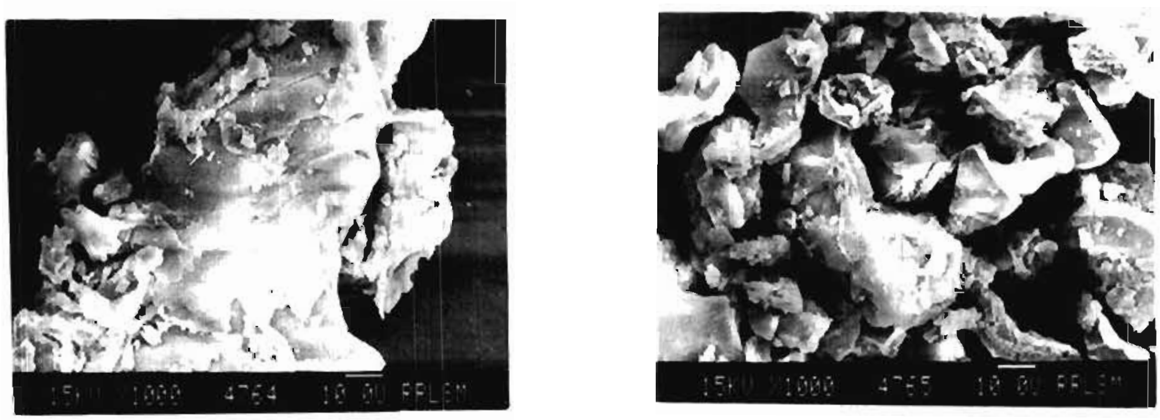
The XRD pattern of various catalysts are given in Fig.47. At 600°C, the XRD shows no phase change but some partial crystallinity is formed when catalyst is calcined at 800°C. The initial pH of the solution had little effect on crystallinity and the oxides formed at initial pH 4 and 6 showed no crystalline nature. When hydroxides are precipitated using urea an amorphous hydroxide is formed, which on calcination produced a fine powder.

5.11.3 Scanning Electron Microscopic Studies

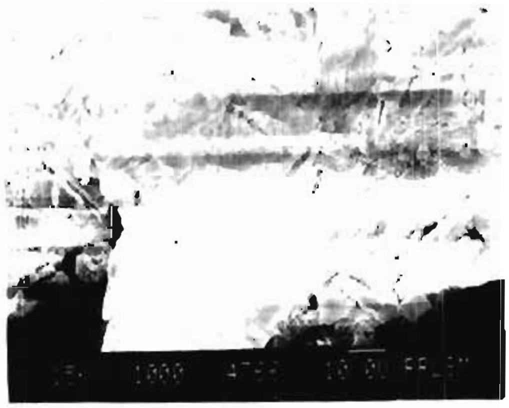
The morphological features of Al_2O_3-Y_2O_3(1:1) precipitated at initial pH 4 and 6 are given in Fig.46. It is quite clear from surface area measurement that hydroxide formed at initial pH 6 is microporous, when pH changes from 4 to 6 an agglomerated form with a partial gel formation occurs which gives a form with high acidity, basicity and activity. Fig.46(c,d,e) present the morphology of catalysts prepared from the hydroxides aged for 3,7 and 14 days. When ageing time changed from 3 to 7 days an agglomerated form of



a. Catalyst prepared at pH4   b. Catalyst preparted at pH6



c. Catalyst aged for 3 days   d. Catalyst aged for 7 days



e. Catalyst aged for 14 days

Fig. 46 SEM of Catalysts.

the catalyst with less pores is formed. When ageing continued for 14 days a partially decomposed gel morphology appeared, with moderate surface area, high acidity, basicity and activity.

5.11.4 Acidic and Basic Properties

Tables 41 to 44 give the acid strength and acid amount of various catalysts used in the study. When calcination temperature increased an increase in acidity was also observed. When catalyst is calcined at 400°C acidity values of 0.0589 m mol/m^2, 0.0044, 0.0021, 0.0030 and 0.0001 m mol/m^2 are obtained at Ho $\leqq$ +6.8, +4, +3.3, +1.5 and -3 respectively. When calcination temperature increased to 600°C acidity values changed to 0.3375, 0.0333, 0.0166, 0.0083 and 0.0029 at respective acid amount of Ho $\leqq$ +6.8, +4, + 3.3, +1.5 and -3.

When pH of the solution changed from 4 to 6, acidity of catalysts decreased. Total acidity changed from 0.5404 m mol/m^2 to 0.2609 m mol/m^2. This may be due to partial gel formation resulting in a tremendous increase in surface area which leads to a reduction in the number of acidic sides per unit area. The acidity of catalysts varied largely with ageing. When catalyst was aged for 3 and 7 days acidity at acid amounts Ho $\leqq$ +6.8, +4 and +3.3 increased and then decreased when ageing time increased to 14 days. This can be explained on the basis of surface area change. Acidity values at Ho $\leq$ +1.5, and -3 showed increase with ageing time. When urea was used as the precipitant total acidity decreased to 0.0245 m mol/m^2 and at all Ho values low acidity was observed.

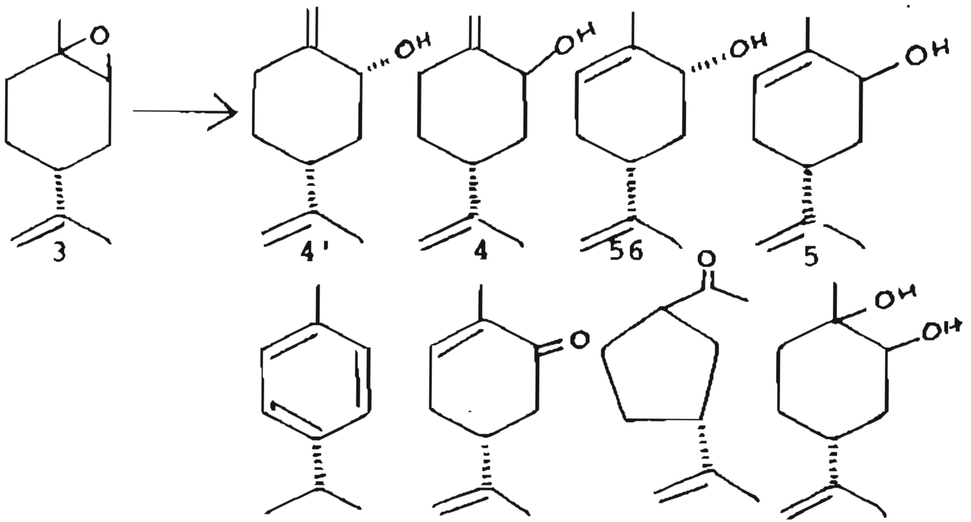
Table 44 give the acidity values of recycled catalysts in m mol/g. Catalyst (11) showed weak acidity at Ho $\leq$ +6.8 and strong acidity at Ho $\leq$ -3.

Basicity of various catalysts are given in Table 45. When calcination temperature increased from 600 to 800°C, total basicity decreased from 4.983 to 3.9063 meq/m^2. Corresponding decrease in basicity at various H-values were also observed. Similarly when pH of initial solution increased, basicity decreased. It is clear from Table 45 that as ageing time increased, total basicity increased from 4.6499 meq/m^2 to 9.941 meq/m^2 and decreased to 7.5552 meq/m^2. A similar trend can be seen at different basic amounts (H_-) when urea is used as the precipitant total basicity is only 1.2819 meq/m^2 but the catalyst showed highest basicity of 0.1709 meq/m^2 at H_-18.4.

5.12 Catalytic Activity

The activity and selectivity of catalysts were checked in the isomerization of (+)-limonene oxide at 110°C. Highest reactivity (90%) was shown by catalyst prepared by urea precipitation. When calcination temperature of catalyst changed from 600 to 800°C, percentage conversion increased from 65 to 75. As the initial pH of the solution changed from 4 to 6 percentage conversion decreased from 75 to 50. Ageing increased reactivity from 66 to 75 and then to 86%.

Over various binary oxides of Al_2O_3-Y_2O_3 (+)-limonene oxide (3) isomerized to give P-cymene (32), trans-exo-carveol(4'),trans-endo-carveol(56),cis-endo-carveol (5), carvone (36), methyl (isopropenyl cyclopentyl) ketone (72), 8(9)-p-menthene 1,2-diol (8)



The percentage conversion varied from 85 to 92 over various recycled catalysts. The main produces obtained in the isomerization are trans and cis-exo-carveol (4' and 4) cis-endo-carveol (5), carvone (36) and 8(9)-p-menthene 1,2 diol (8). The activity and selectivity of various catalysts are given in Tables 46 and 47.

Table 46

Activity and Selectivity of Various Catalysts for (+)-Limonene Oxide Isomerization

Catalyst	Conversion (%)	Product %						
		4'	5	56	36	8	72	32
Al_2O_3-Y_2O_3-A_1	65	10	-	8	7	45	-	-
Al_2O_3-Y_2O_3-A_2	75	13	4	14	9	32	-	-
Al_2O_3-Y_2O_3-A_3	75	10	8	-	5	32	-	-
Al_2O_3-Y_2O_3-A_4	50	2	5	20	6	32	-	-
Al_2O_3-Y_2O_3-A_5	66	7	5	9	4	43	-	1
Al_2O_3-Y_2O_3-A_6	75	5	3	6	3	52	-	2
Al_2O_3-Y_2O_3-A_7	86	3	4	5	-	70	-	2
Al_2O_3-Y_2O_3-A_8	90	-	9	-	9	-	42	-
Al_2O_3-Y_2O_3 (Calcined at 400°C)	58	10	4	8	5	65	-	-

Table 47

Activity and Selectivity of Various Recycled Catalysts

Catalyst	Conversion	Product %				
		4	4'	5	36	8
Catalyst II	85	5	4	7	3	51
Catalyst III	90	8	5	10	5	38
Catalyst IV	92	8	6	10	5	57
Catalyst V	89	15	8	17	5	40

5.12.1 Trans-exo-carveol (4')

The yield of trans-exo carveol varied from 2 to 13% over various catalysts. Maximum yield (13%) was produced over Al_2O_3-Y_2O_3 (1:1) calcined at 800°C and minimum (2%) was produced over Al_2O_3-Y_2O_3 (1:1) precipitated at pH 6. Al_2O_3-Y_2O_3 (1:1) calcined at 600°C and Al_2O_3-Y_2O_3(1:1) produced at pH 4 also produced 10% yield of alcohol.

An attempt has been made to correlate the acidity and basicity at various Ho values to the yield of alcohol as shown in Figs. 48 and 49. The variation in the percentage production of alcohol with acid amount is not regular and hence no useful correlation can be obtained. Such observation can be obtained in the case of basicity also.

5.12.2 Trans-endo-carveol (56)

The yield of trans endo carveol ranged from 5 to 20% over various catalysts. Maximum yield 20% was produced over Al_2O_3-Y_2O_3 (1:1) produced at initial pH 6. When calcination temperature of catalyst changed from 600 to 800°C, the yield of alcohol increased from 8% to 14%.

The variation of acidity and basicity of catalyst with yield of alcohol was given in Figs. 48 and 49. From the figure it is observed that the variation of acidity and basicity with alcohol yield is irregular.

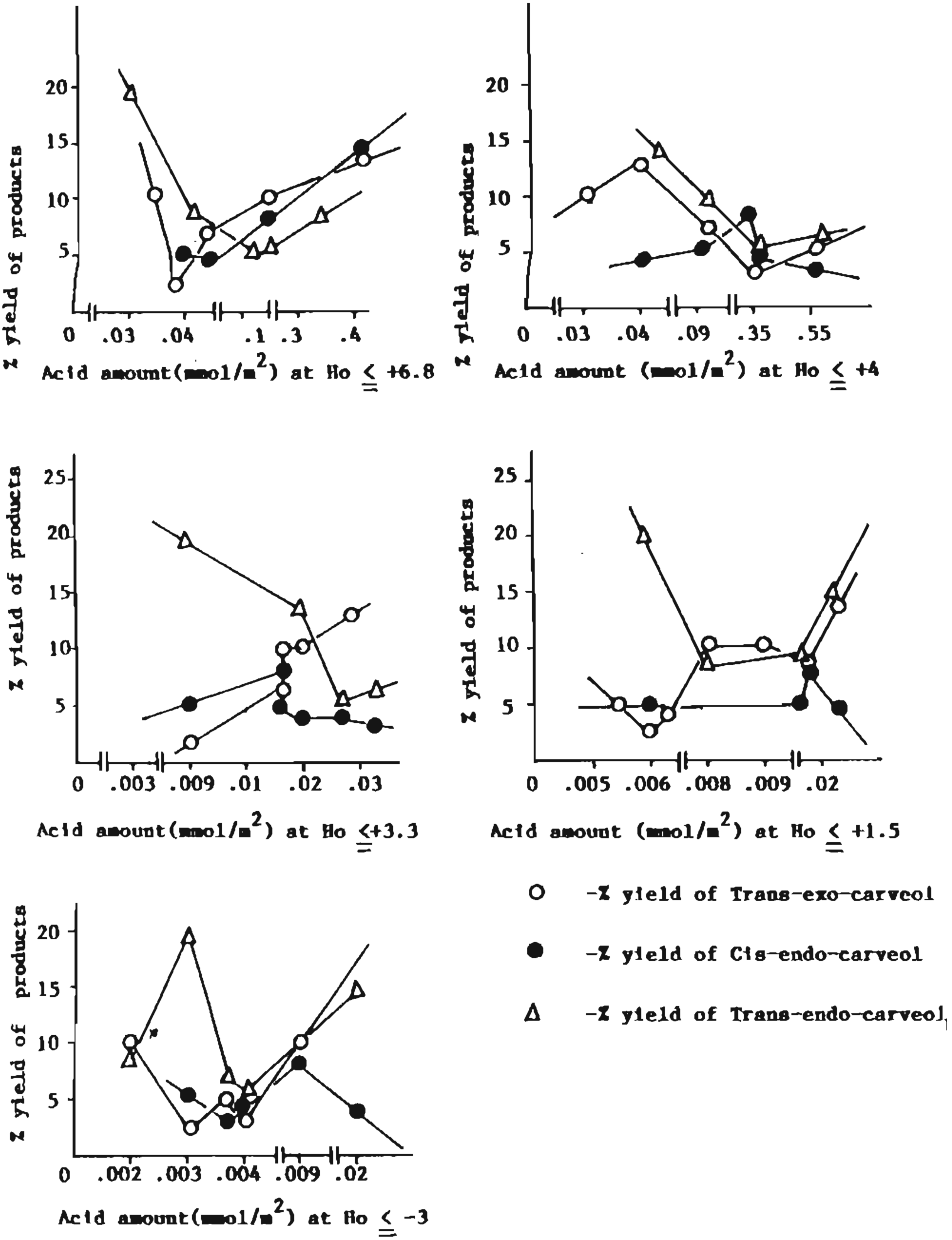


Fig.48 Variation in the percentge yield of various products with acid amount

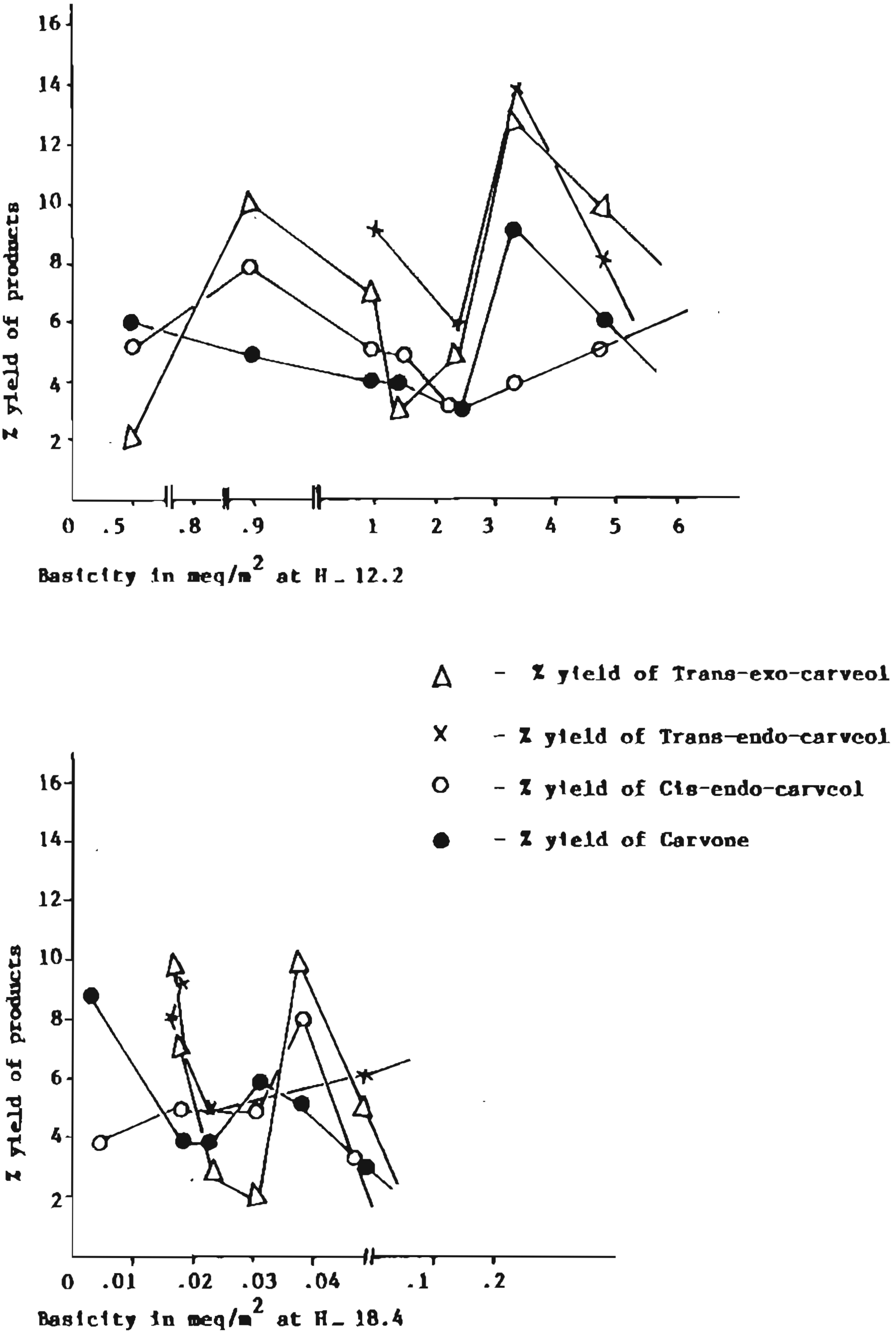


Fig.49 Variation in the percentage yield of products with basicity

5.12.3 Cis-endo-carveol (5)

Cis-endo-crveol is produced in 3 to 9% over various catalysts. Maximum yield 9% was observed over Al_2O_3-Y_2O_3 made by urea precipitation. Cis-endo-carveol was produced in 17% yield by the recycled catalyst in the 5th cycle. In various other cycles yield varied from 7 to 10%.

The variation of acidic and basic amounts with percentage production of cis-endo-carveol is given in Figs. 48 and 49. As shown in figure no direct relation involving allyl alcohol production and acidity or basicity is obtainable from the data.

5.12.4 Cis-exo-carveol (4)

This alcohol is produced in 4 to 8% over various recycling reactions and maximum yield 8% was observed in the 5th cycle.

5.12.5 Carvone (36)

Carvone is produced in 3 to 9% over various catalysts Al_2O_3-Y_2O_3 (1:1) calcined at 800°C and Al_2O_3-Y_2O_3(1:1) produced by urea precipitation produced 9% yield of carvone. Carvone is produced in 3 to 5% yield over various recycled catalysts.

The acidity and basicity of catalysts were correlated to percentage yield of carvone over various catalysts. No correlation can be observed for all catalysts.

5.12.6 8,9-p-menthene 1,2-diol (8)

Diol is the major product produced over various catalysts. Except Al_2O_3-Y_2O_3 (1:1) prepared by urea all other catalysts produced diol in 32 to 70%. Al_2O_3-Y_2O_3(1:1) calcined at 400°C yielded 65% diol while the percentage decreased from 45 to 32 when calcination temperature changed from 600 to 800°C. Maximum yield 70% was observed over Al_2O_3-Y_2O_3 (1:1) aged for 14 days.

Along with these major products mentioned above some minor products like p-cymene (32) was also produced in the reaction. Al_2O_3-Y_2O_3 (1:1) made by urea precipitation alone produced methyl (isopropenyl cyclopentyl) ketone (72) in 42% yield.

5.13 Conclusion

Studies on the preparation of alumina rare earth oxide catalysts under various preparation conditions show that the morphology and surface area largely controlled by amounts of amorphous hydroxide and various partially crystalline phases present in the medium. This in turn is controlled by pH at which precipitation is carried out and ageing of the precipitate.

Calcination temperature largely influenced the catalytic activity. When Al_2O_3-Y_2O_3 (1:1) prepared at 400°C was compared to that prepared at 600°C and 800°C a large increase in activity was observed. The percentage conversion of reactants increased from 58 to 65 and then to 75. The product formed from the three catalysts were same. There are variation in the percentage yield of various products. The yield of various products increased with increase in the calcination temperature, but a sharp decrease in the percentage yield of diol was observed. Yield of diol decreased from 65 to 32. Al_2O_3-y_2O_3 (1:1) prepared by urea precipitation showed large difference in activity and selectivity from the rest of catalysts. This catalyst showed highest activity and maximum selectivity (42%) for ketone formation.

CHAPTER VI

SUMMARY AND FUTURE PERSPECTIVES

6.1 Summary

Aluminium-rare earth binary oxide catalysts were prepared and their activity and selectivity were determined in the transformations of α, β-pinene oxides, (+), (-)-limonene oxides, 3-carene oxide and ar-curcumene oxide. The results obtained in the study are presented in this work.

Catalysts like Al_2O_3-Y_2O_3, Al_2O_3-Sm_2O_3, Al_2O_3-Pr_6O_{11}, Al_2O_3-Eu_2O_3 and Al_2O_3-Nd_2O_3 were prepared in 1:1 (w/w) ratio. Surface area, pore size distribution, acidity and basicity of catalysts were measured. XRD, TGA, ESCA and MAS ^{27}Al NMR of the catalysts were recorded. From thermogravimetric data it is clear that rare earth oxides shift the decomposition temperature of catalysts to lower ranges. The low temperature calcination, 400°C is insufficient for particle coarsening and can be seen from XRD studies. The catalysts showed wide pore size distribution, acidity as well as basicity.

The activity and selectivity of catalysts varied with epoxide used for transformation studies. Carbonyl compounds like compholenaldehyde, pinocarvone, myrtanal, and 3,6,6-trimethyl bicyclo [3.1.0] hexane carboxaldehyde were the major products formed over α,β-pinene oxides and 3-carene oxide. (+)-Limonene oxide produced more exo-allylic alcohol while (-)-limonene oxide yielded more endo-allylic alcohol. Major product formed from ar-curcumene epoxide was an allylic alcohol. An attempt to correlate catalytic acidity and basicity with yield of various products were made.

Al_2O_3-Y_2O_3 catalysts in different compositions like 9:1, 7:3, 1:1, 3:7 and 1:9 were prepared and characterised by surface area, pore size distribution, acidity and basicity measurements. SEM, XRD, TGA, MAS ^{27}Al NMR of catalysts were recorded. As the yttrium content in catalyst increased partial crystallinity and microporosity were introduced in to the catalyst. Acidity decreased when composition changed from Al_2O_3-Y_2O_3(9:1) to Al_2O_3-Y_2O_3 (1:1). Catalyst samples with more Y_2O_3 showed less acidity and basicity. Catalytic activity in the transformation of (+)-limonene oxide decreased as the composition of catalyst changed from Al_2O_3-Y_2O_3(9:1) to Al_2O_3-Y_2O_3 (1:9).

Different modes of preparation were adopted in making Al_2O_3-Y_2O_3(1:1) catalysts and their activity determined in the transformation of (+)-limonene oxide. Catalytic acidity and activity were enhanced by higher calcination temperature. Ageing of the precipitated hydroxide influenced catalyst's morphology, acidity and basicity. Ageing produced an increase in catalytic activity with increased production of diol. Al_2O_3-Y_2O_3 (1:1) prepared by urea precipitation showed highest catalytic activity.

6.2 Suggestions for Future Work

The binary oxide catalysts, alumina-rare earth oxides has not been reported in the transformation of terpenyl oxiranes till the present work. Even though the expected products of perfumery value were only obtained in lower amounts those catalysts show promise. The formation of allylic alcohols were favoured by these catalysts. Attempts should be made to make catalysts with more specificity to obtain important perfumery chemicals by changing the mode of preparation, calcination, composition etc.

The surface characteristics of the catalysts were determined after the catalysts were prepared in this work. An indepth interpretation of TGA data may lead to the optimum calcination temperature and possible information on the acidic and basic properties of the catalysts. This should be carried out before actually making the catalysts. Coprecipitation method has been found to be quite good in high surface area and wide pore size. Latest technique of preparing fine powders like sol-gel technique may be adopted for making the catalysts.

All the epoxides studied in this work were mixtures of cis-and trans-isomers. It could be beneficial to carry out *reactions with single* epoxides for proper understanding of the approach of the substrate molecule with catalyst surface and thereby to the products.

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