Catalytic transformation of (+)−limonene oxide over binary oxide catalysts of alumina-rare earths

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The transformation reactions of (+)-limonene oxide over binary oxides 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 at 110°C and 140°C are discussed. The activity of single oxides like Al_2O_3, Eu_2O_3, Nd_2O_3 and Y_2O_3 used for the transformation reaction is studied at 110°C. Among the binary oxides, Al_2O_3-Eu_2O_3 show maximum activity for epoxide transformation. Methyl (3-isopropenyl cyclopentyl) ketone (**4**) and carvone (**5**) are the major products formed over binary oxides at higher reaction temperture.

Introduction

Compounds formed from the rearrangement of epoxides are valuable intermediates in organic synthesis[1-3]. The naturally occurring terpene hydrocarbons can easily be converted to epoxide economically and their further transformation by heterogeneous catalysis can provide compounds of value. The transformation reactions of limonene oxide have been studied over a number of solid catalysts[4-8]. The decomposition, deoxygenation and addition of limonene oxide has been investigated by a number of workers[9-11] and its rearrangements were reported over various types of alumina[12,13]. Alumina contained Bronsted and Lewis acid sites as well as basic sites. The present work has been undertaken to investigate the variation in the activity of alumina by the addition of rare earth oxides. Binary oxides 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 were used as catalysts. For comparing the catalytic performance, single oxides like Al_2O_3, Y_2O_3, Eu_2O_3 and Nd_2O_3 were also used for transformations at 110°C. Catalyst acidity was correlated to the yield of major products formed in the transformation reaction.

Materials and Methods

Materials. (+)-Limonene oxide (a 1:1 mixture of *cis* and *trans* epoxide) was supplied by Aldrich Chemical Co., USA. Toluene and xylene were guaranteed reagents redistilled over sodium metal. Single oxides and binary oxides 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 were prepared as hydroxides by coprecipitation from corresponding nitrates using NH_3. The hydroxides were aged for 20h, washed, filtered, dried at 130°C for 24h and calcined at 400°C in air for 5h.

Methods. The catalysts were completely characterised by methods like XRD, TGA, BET, XPS and MAS ^{27}Al NMR and is reported elsewhere.[14] Catalyst acidity was estimated by titration with *n*-butyl amine and basicity of the catalysts were determined by titration with benzoic acid and the results are summarised in Table I[15,16]. Acidity of catalysts like Al_2O_3-Pr_6O_{11} and Pr_6O_{11} could not be determined due to the dull green colour of the catalyst.

Reaction procedure and product identification. Catalyst (1g) and epoxide (1.3 mmole) were refluxed in toluene (10mL) and reaction rate was

Table I—Acidity and basicity of various catalysts

Catalysts	Acid amounts in mmole/m^2 at various acid strengths					Basicity in mmole/m^2 at different basic strengths	
	+6.3	+4	+3.3	+1.5	−3	+12.2	+15
Al_2O_3	0.115	0.115	0.103	0.000	—	—	—
Y_2O_3	0.089	0.331	0.065	—	—	—	—
Eu_2O_3	0.071	0.001	0.023	0.000	—	—	—
Nd_2O_3	0.031	0.056	0.013	0.001	—	—	—
Al_2O_3-Y_2O_3	0.059	0.004	0.002	0.003	0.000	0.023	0.045
Al_2O_3-Eu_2O_3	0.113	0.499	0.035	0.038	0.008	0.059	0.286
Al_2O_3-Sm_2O_3	0.092	0.437	0.029	0.004	0.007	0.124	0.132
Al_2O_3-Nd_2O_3	0.107	0.509	0.012	0.007	0.002	0.121	0.241

frequently monitored by TLC. After completion of reaction (12h) reaction mixture was filtered and catalyst extracted with methylene chloride under reflux. The reaction filtrate and catalyst extract combined and solvent was removed *in vaccuo.* Same method was followed for other catalysts and for reaction at 140°C. Reaction products were analysed by GLC, GC-MS and identified by comparing relative retention times with authentic samples. The authentic samples of *trans-* and *cis*-exo carveols (**2,3**) and methyl (3-isopropenyl cyclopentyl) ketone (**4**) were prepared by known methods[18,19]. A standard sample of carvone was supplied by Fluka and limonene diol was prepared by the hydrolysis of limonene oxide. GLC was carried out on a 5840A model Hewlett Packard gas chromatograph: Column OV17 (10%) 1.8m in length, id 3.1mm, column temperature 80 to 200°C at a rate of 10°C/min using an FID detector injector temperature 250°C FID temperature 250°C.

GC-MS analysis was performed on a varion 3400 Incos 50 mass spectrometer, Column DB-5, 30m in length, i.d. 0.25mm, column temperature 60 to 200°C at a rate of 5°C/min. The m/z data obtained for various compounds are: **2**: 41(100), 55, 67, 79, 91, 109, 119, 134, 105, 123; **3**: 41(100), 81, 67, 55, 107, 93, 121, 136, 152; **4**: 41 (100), 55, 109, 84, 91, 69, 77, 119, 105, 134, 123; **5**: 82(100), 54, 41, 93, 108, 79, 58, 67; **6**: 43(100), 71, 67, 55, 82, 108, 88, 137, 152, 119, 101. The mass spectral data were compared to NBS mass spectral library and literature[20].

Results and Discussion

The XRD data clearly indicated that the single oxide catalysts used in the present study showed some crystallinity and binary oxides showed amorphous nature[21]. Single oxides and binary oxides were precipitated as hydroxides from corresponding nitrates. The hydroxides were used for thermal analysis and it is seen that rare earths showed a tendency to bring down the decomposition temperature of aluminium hydroxide between 286 and 296°C. The hydroxides of yttrium, neodymium and europium showed a thermal decomposition resulting in a slow hydroxyl removal from them (Figure 1). The activity of single oxides can be easily explained by the presence of hydroxyls which act as weak acid sites. Single oxides showed weak acidity in the Ho range +6.8 to +1.5 but no basic sites are observed. All binary oxides showed weak to moderate acidity in the Ho range of +6.8 to −3.0 and basic strength varying between $pkBH$ value 12.2 and 15 and the
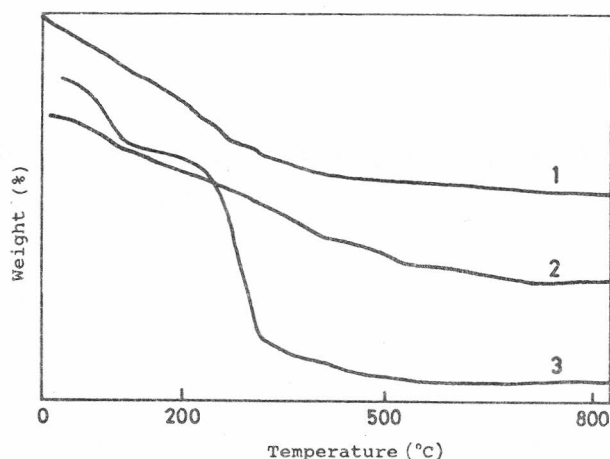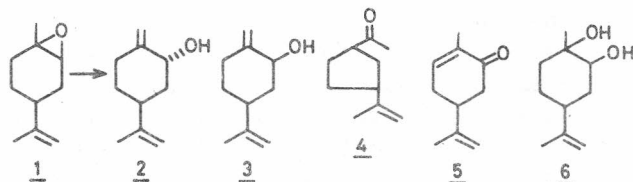

Figure 1—Thermogravimetric curves of (1) hydroxide of yttrium; (2) hydroxide of neodymium; (3) hydroxide of europium

results are summarised in Table I. Coprecipitation increased the number of stronger acidic sites on binary oxide surface. New basic sites were also created on the surface of binary oxides. Details of complete characterisation of the binary oxide catalysts are given elsewhere[14].

The major compounds obtained from (+)−limonene oxide (**1**) in this transformation reaction are *trans* and *cis*-exo-carveols (**2,3**), methyl (3-isopropenyl cyclopentyl)ketone (**4**), carvone (**5**) and 8,9-*p*-menthene-1,2-diol (**6**). The activity and selectivity of various catalysts at 110°C for 12h and 140°C for 5h are given in Tables II and III. At 140°C the reaction was complete (no significant

Table II—Activity and selectivity of catalysts at 110°C (for 12h) for the major constituents identified

Catalyst	Conversion (%)	Selectivity(%)				
		2	3	4	5	6
Al_2O_3	95	12	—	—	20	60
Y_2O_3	60	21	—	—	30	18
Eu_2O_3	69	28	—	—	49	10
Nd_2O_3	62	28	—	—	43	17
Al_2O_3-Y_2O_3	65	12	10	9	9	30
Al_2O_3-Eu_2O_3	78	35	20	20	10	14
Al_2O_3-Pr_6O_{11}	76	33	—	20	10	20
Al_2O_3-Sm_2O_3	70	22	5	10	14	25
Al_2O_3-Nd_2O_3	72	30	15	15	15	30

Table III—Activity and selectivity of catalysts at 140°C for 5h for the major constituents identified

Catalyst	Conversion %	Selectivity(%)				
		2	3	4	5	6
Al_2O_3-Y_2O_3	53	24	10	18	20	24
Al_2O_3-Eu_2O_3	81	25	18	16	28	10
Al_2O_3-Pr_6O_{11}	73	24	9	14	24	8
Al_2O_3-Sm_2O_3	75	19	10	18	22	9
Al_2O_3-Nd_3O_3	80	17	12	19	24	10

increase in the yield of products) but lower reaction temperature required more reaction time for completion.

At 110°C, the percentage transformation of epoxide varied from 65 and 78 and a rise in reaction temperature to 140°C produced a small increase in the percentage conversion of epoxide in the case of Al_2O_3-Eu_2O_3, Al_2O_3-Sm_2O_3 and Al_2O_3-Nd_2O_3. Al_2O_3-Eu_2O_3 produced maximum conversion of epoxide and Al_2O_3-Y_2O_3 produced the minimum. *Trans* and *cis*-exo carveols (**2,3**) are the major products formed in the transformation reaction over Al_2O_3-Eu_2O_3, Al_2O_3-Pr_6O_{11} and Al_2O_3-Nd_2O_3. Single oxides like Eu_2O_3 and Nd_2O_3 showed less conversion of epoxide compared to Al_2O_3-Eu_2O_3 and Al_2O_3-Nd_2O_3. Among the allyl alcohols formed in the reaction *trans*-exo-carveol (**2**) is the major one. The yield of **2** varied from 12 to 35% at 110°C and 17 to 25% at 140°C. Al_2O_3-Eu_2O_3 and Al_2O_3-Pr_6O_{11} produced maximum yield of allyl alcohol (**2**).

Alumina contains both Lewis and Bronsted acidity on its surface. Removal of hydroxyl groups by calcination from the catalyst surface leaves some electron deficient centers on catalyst surface. These centers act as adsorption site for the epoxide. The mechanism for the formation of various products from epoxide is illustrated in Scheme I. The epoxide gets attached to an electron deficient centre on catalyst surface through oxygen atom. The epoxide ring opens up followed by the formation of tertiary carbocation which rearranges to different products. In Figure 2 the variation in the percentage formation of *trans*-exo-carveol (**2**) (for reaction at 110°C) with acidity of all catalysts for Ho +6.8 and +1.5 is illustrated. The yield of *trans*-exo carveol (**2**) increased with increase in acidity.

Except Al_2O_3-Pr_6O_{11} all catalysts yielded *cis*-exo-carveol (**3**) at 110°C and the yield varied from 5% to 20%. Compared to the yield of alcohol (**2**),

A: Acidic site   B: Basic site
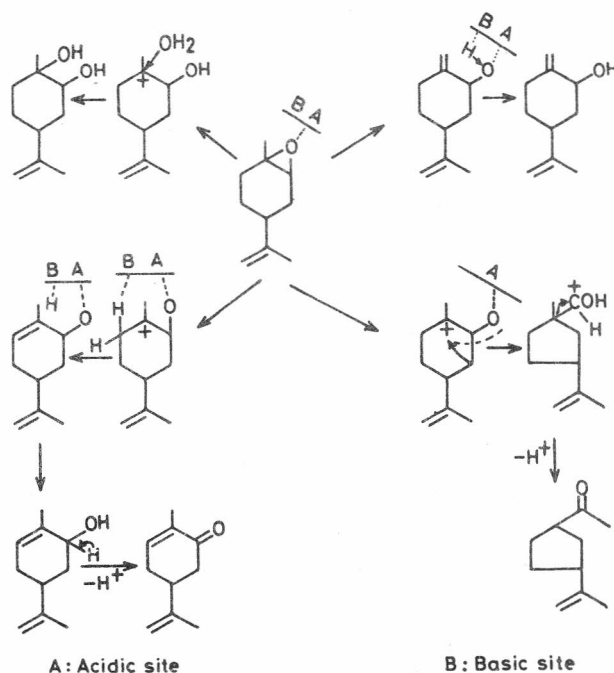
Scheme I

the yield of **3** is less in all reactions studied. The epoxide (**1**) used in the present investigation is a 1:1 mixture of *cis* and *trans* isomers and the *trans* epoxide may be relatively more reactive and yield more *trans* alcohol (**2**). Another reason for the formation of *trans* alcohol is that abstraction of a primary hydrogen which is more facile than a secondary one. There is no correlation with the yield of alcohol (**3**) with acidity.

Methyl-(3-isopropenyl cyclopentyl) ketone (**4**) was formed in the transformation reaction. At 110°C. Its percentage yield varied from 9 to 20. As reaction temperature increased to 140°C, the yield increased in the case of Al_2O_3-Eu_2O_3 and Al_2O_3-Pr_6O_{11}. The variation in the yield of ketone (**4**) formed at 140°C with catalyst acidity at Ho values +3.3 and -3 is illustrated in Figure 3. At 140°C, with increase in acidity at Ho +3.3 and -3, the yield of ketone (**4**) increased.

The yield of carvone (**5**) varied from 9 to 20% at 110°C, the maximum being in the case of Eu_2O_3 (30%). At 140°C, Al_2O_3-Eu_2O_3 produced maximum yield of carvone (28%). An increase in reaction temperature from 110°C to 140°C resulted in an increase in the yield of carvone. In Figure 4 the gradual increase in the yield of carvone with acidity of all catalysts at Ho + 6.8 and + 1.5 is illustrated (140°C). Besides these major products Al_2O_3-Y_2O_3, Al_2O_3-Sm_2O_3, Al_2O_3-Pr_6O_{11} and Y_2O_3 yielded some unidentified compounds in minor amounts.
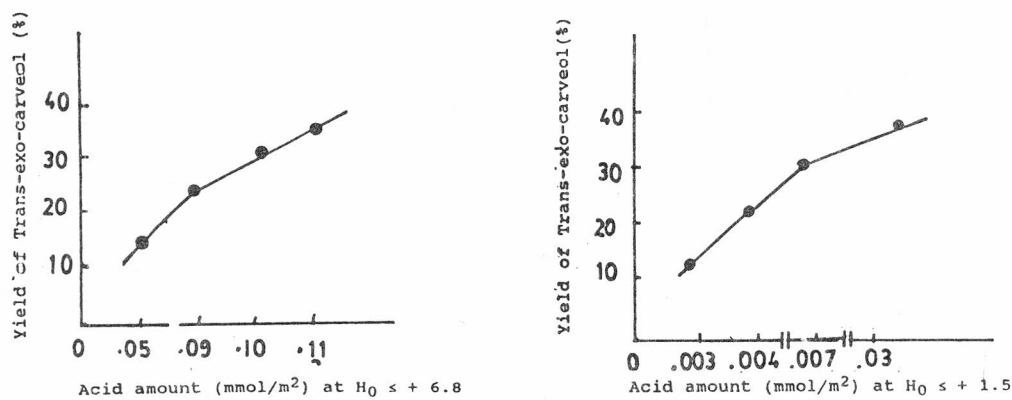
Figure 2—Variation in the percentage yield of *trans*-exo-carveol (2) with acid amount of all catalysts in mmole/m^2 at Ho + 6.8 and +1.5 (reaction at 110°C).
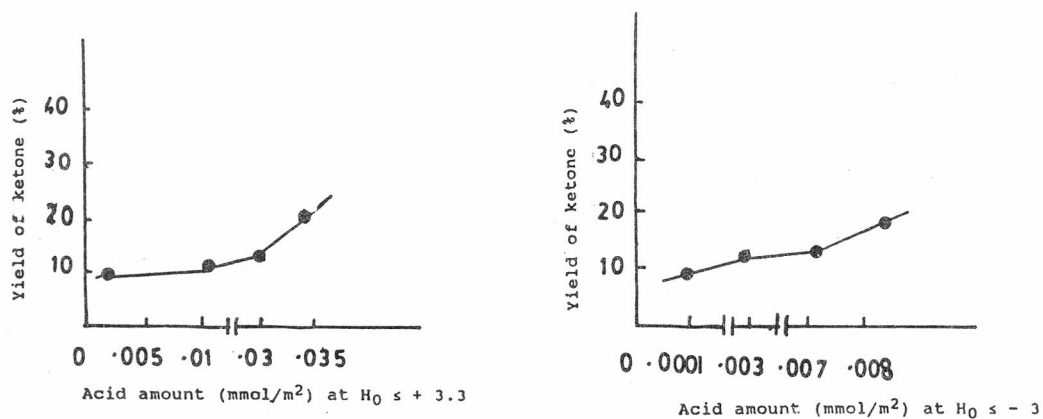

Figure 3—Variation in the percenage yield of ketone (4) with acid amount of all catalysts in mmole/m^2 at Ho +3.3 and −3 (reaction at 140°C).
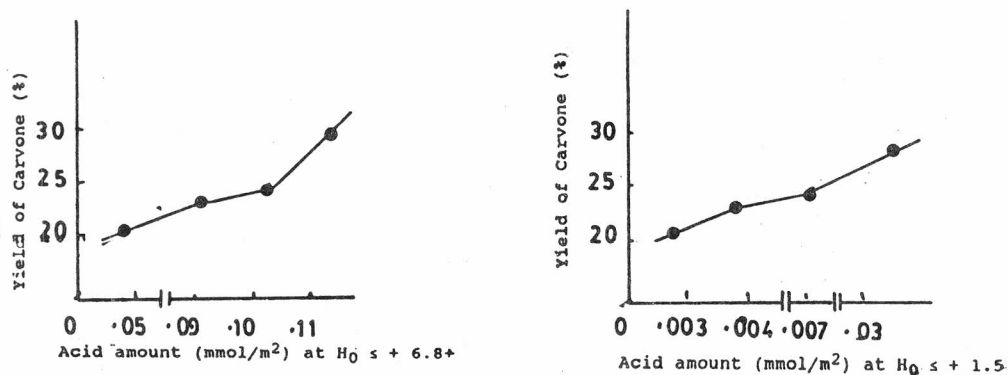

Figure 4—Variation in the percentage yield of carvone (5) with acid amount of all catalysts in mmole/m^2 at Ho +6.8 and +1.5 (reaction at 110°C).

Conclusion

Alumina prepared in the present study yielded diol (**6**) as the major product. Single oxides like Y_2O_3, Eu_2O_3 and Nd_2O_3 mainly yielded carvone (**5**). The activity and selectivity of binary oxides of alumina-rare earths are different from single oxides. Binary oxides of Al_2O_3 with oxides like Eu_2O_3, Nd_2O_3, Nd_2O_3 and Pr_6O_{11} are found to be more efficient catalysts than single oxides for the transformation of (+)-limonene oxide. At 110°C allyl alcohols are the major products obtained from binary oxides and at 140°C carbonyl compounds are the major products.

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