Part II: Transformations of α and β-Pinene Oxides over Binary Oxide Catalysts of Alumina–Rare Earth Oxides

Janakiamma Jayasree and Cadavallore S. Narayanan*

Regional Research Laboratory (CSIR), Thiruvananthapuram, Kerala-695019, India

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The catalytic activity of binary oxides of Al_2O_3–Eu_2O_3, Al_2O_3–Sm_2O_3, Al_2O_3–Nd_2O_3, Al_2O_3–Pr_6O_{11}, and Al_2O_3–Y_2O_3 were checked in the transformations of α and β-pinene oxides. Al_2O_3–Eu_2O_3 and Al_2O_3–Nd_2O_3 are found to be best catalysts for α-pinene oxide isomeriztion. Among the oxiranes, α-pinene oxide showed more activity mainly yielding 2,2,3-trimethyl cyclopentene-1-acetaldehyde. β-pinene oxide produced *trans*-myrtanal and myrtanol.

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. There are reports on the use of solid acid base catalysts for the transformation of oxiranes to useful products. In our ongoing efforts to obtain flavor compounds of value, chiral pool of terpenes like α and β-pinenes abundantly available from natural sources were utilized. Sukh Dev has extensively studied the isomerization of α and β-pinene oxide on silica gel, Al_2O_3 and doped Al_2O_3.[1a,1b,1c] Pinocamphone was produced on pyrolysis of α-pinene oxide over iron[2] or a sealed tube.[3] Tanabe has investigated α-pinene oxide isomerization over various solid acid and basic catalysts.[4] Synthetic zeolites and acid adsorbed alumina and silica isomerized α-pinene oxide to various products.[5,6] Alumina showed Brönsted and Lewis acidity, as well as basicity. The present study was carried out to see how the acidic and basic sites on binary oxide catalyst surface influenced the epoxide transformations. An attempt to correlate acidic and basic property and product distribution was also made.

Experimental

Binary oxide catalysts 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 in the present study. They were prepared by coprecipitation from corresponding nitrates. The hydroxides were aged for 20 h, washed and calcined at 400 °C in air for 5 h. The surface characteristics, thermal stability, acidity and basicity of catalysts were determined using techniques like XRD, ESCA, MAS ^{27}Al NMR, BET, and TGA. This part of the study is included in the Part I of the series of publication.

Materials: α-Pinene oxide was prepared by the monoperpthalic acid oxidation of (+) α-pinene and β-pinene oxide used was obtained from Aldrich Chemical Company, USA.

Reaction Procedure: α-Pinene oxide (1.3 mmol) and Al_2O_3–Y_2O_3 (1 g) were refluxed in 10 ml benzene. Reaction course was monitored by TLC for 15 h. Reaction mixture was filtered and then catalyst was washed and extracted with methylene chloride. All extracts were combined together and solvent was removed. The same procedure was followed at 80, 110, and 140 °C. β-Pinene oxide isomerization was carried out in a similar way at 80, 110, and 140 °C.

Identification of Products: The products in these reactions were analysed by GLC and GC-MS. Constituents were identified by comparing the relative retention times with authentic samples. Linalyl acetate was used as inter-

Table 1. MS Values Obtained for Various Compounds

Compound	MS values
II	108(100), 93, 41, 67, 95, 43, 55, 91
III	41(100), 55, 91, 70, 79, 119, 105, 134
IV	41(100), 55, 69, 83, 95, 91, 110
V	81(100), 53, 108, 41, 150, 135, 122, 69, 39, 27
VI	41(100), 54, 82, 95, 67, 91, 109
VII	41(100), 95, 109, 53, 91, 67, 43, 55, 77, 93
VIII	41(100), 54, 82, 93, 44, 51, 79, 77, 95, 91, 108
X	41(100), 79, 55, 67, 86, 123, 91, 59, 114, 105, 133
XI	79(100), 41, 67, 107, 55, 85, 93, 122, 113, 135, 153
XIII	79(100), 91, 108, 119, 41, 93, 92, 43, 121, 152

Table 2. Acidity Distribution of Various Catalysts in mmol m^{-2} at Various Acid Strength

Catalyst	Acid amount in mmol m^{-2} (H_o)				
	+6.8	+4	+3.3	+1.5	−3
Al_2O_3–Y_2O_3	0.059	0.004	0.002	0.003	0.000
Al_2O_3–Nd_2O_3	0.107	0.509	0.012	0.007	0.003
Al_2O_3–Sm_2O_3	0.092	0.438	0.029	0.004	0.007
Al_2O_3–Eu_2O_3	0.114	0.499	0.035	0.038	0.008

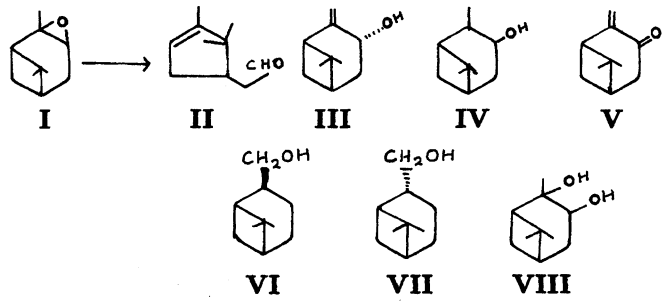
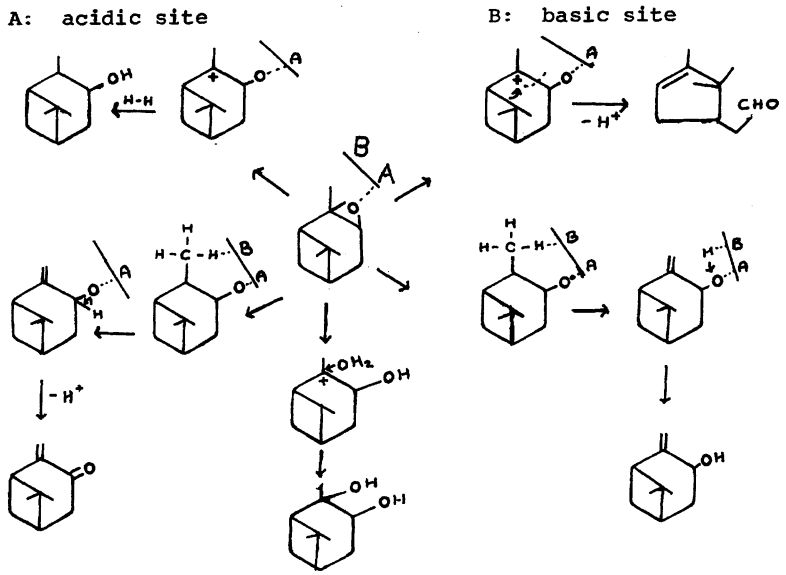


Chart 1.



Scheme 1.

Table 3. Activity and Selectivity of Various Catalysts for Transformations of α-Pinene Oxide

Catalyst	Conversion	Selectivity/%						
	%	II	III	IV	V	VI	VII	VIII
Al_2O_3–Y_2O_3[a]	50	29	11	14	25	—	—	—
Al_2O_3–Sm_2O_3[a]	62	34	16	20	19	—	—	—
Al_2O_3–Eu_2O_3[a]	82	35	—	21	23	10	—	—
Al_2O_3–Nd_2O_3[a]	83	31	17	21	20	—	—	—
Al_2O_3–Pr_6O_{11}[a]	65	40	17	16	15	—	—	—
Al_2O_3–Y_2O_3[b]	80	20	10	20	4	4	—	4
Al_2O_3–Sm_2O_3[b]	90	18	26	18	19	3	—	—
Al_2O_3–Eu_2O_3[b]	94	31	11	21	17	6	—	—
Al_2O_3–Nd_2O_3[b]	91	25	16	20	14	5	—	—
Al_2O_3–Pr_6O_{11}[b]	93	21	15	17	13	5	—	7
Al_2O_3–Y_2O_3[c]	97	20	10	13	15	—	—	—
Al_2O_3–Sm_2O_3[c]	96	18	22	16	17	—	—	6
Al_2O_3–Eu_2O_3[c]	100	46	—	16	12	—	6	4
Al_2O_3–Nd_2O_3[c]	100	20	12	20	22	—	4	—
Al_2O_3–Pr_6O_{11}[c]	97	29	11	18	18	4	3	—

a) Reaction at 80 °C. b) Reaction at 110 °C. c) Reaction at 140 °C.

nal standard in GLC. For identification, compounds **II**, **III**, **V**, **VII**, and **XII** were prepared by methods reported in literature.[7—9] Compounds **IV**, **VII**, **X**, and **XI** were supplied by Fluka, A. G Chem. USA.

GLC analysis was carried out in 5840 A model Hewlett Packard Gas Chromatograph, column 1.8 m length, 3.1 mm

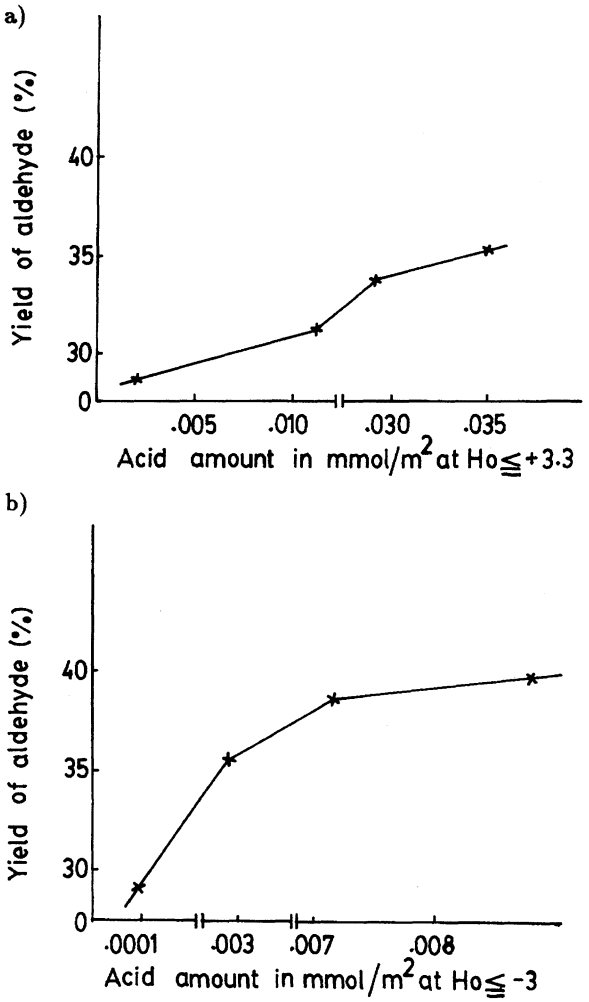


Fig. 1. Variation in the yield of aldehyde (**II**) with acid amount.

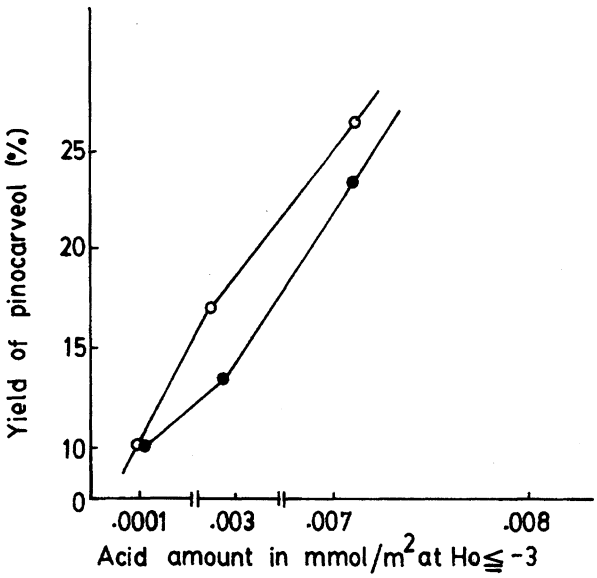


Fig. 2. Variation in the percentage yield of *trans*-pinocarveol (**III**) with acid amount at $H_o \leq +3.3$ and -3. -o- Reaction at 110 °C; -•- Reaction at 140 °C.

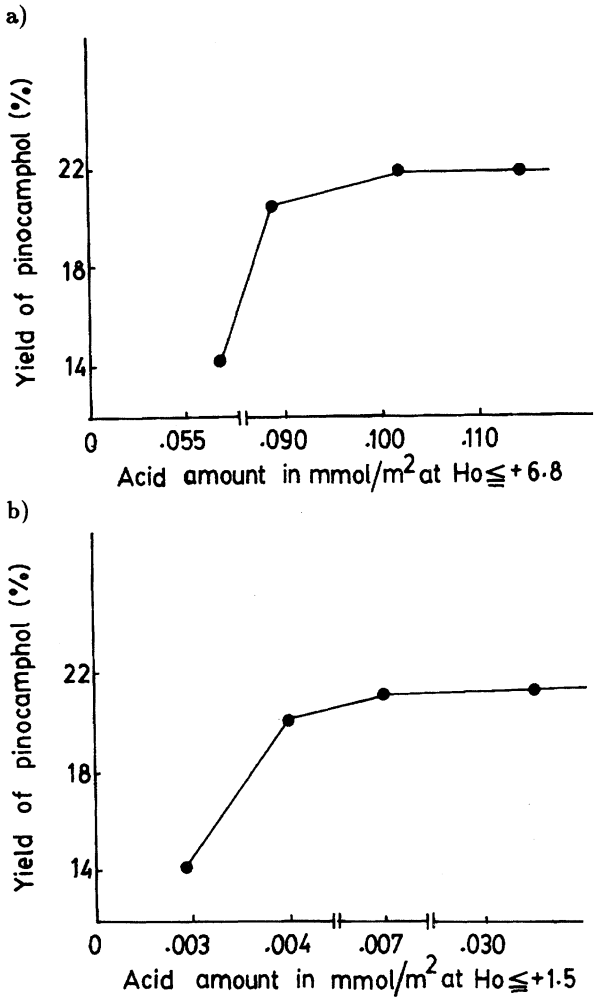


Fig. 3. Variation in the percentage yield of pinocamphol (**VI**) with acid amount for reaction at 80 °C.

i.d. OV 17 (10%) on acid washed WHP, carrier gas N_2, flow rate 20 ml min, detector FID, column temperature programme from 80–200 °C at the rate of 5 °C min^{-1} and kept at 200 °C for 10 min. Injector temperature was kept at 250 °C, FID temperature was 300 °C.

GC-MS analysis was carried out in a Varian 3400 Incos-50 spectrometer, Column DB-5, 30 m length, i.d. 0.25 mm, carrier gas helium. Temperature programme was from 60–200 °C at the rate of 5 °C min^{-1}. MS data obtained for various compounds are given in Table 1.

Results and Discussion

Transformation of α-Pinene Oxide: Over various catalysts α-pinene oxide gave the following products (Chart 1), a ring contracted aldehyde, 2,2,3-trimethyl cyclopentenyl acetaldehyde (**II**), trans-pinocarveol (**III**), pinocamphol (**IV**), pinocarvone (**V**), *cis*- and *trans*-myrtanol (**VI**, **VII**), and pinene diol (**VIII**).

Table 2 represents the acid amount expressed in mmol m^{-2} of various catalysts used in the present study. Table 3 gives the activity and selectivity of the catalysts. From the data given in Tables 2 and 3 it is clear that weak and moderate acid sites on catalyst surface

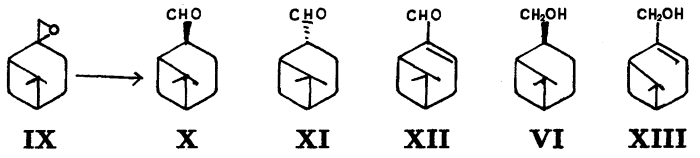
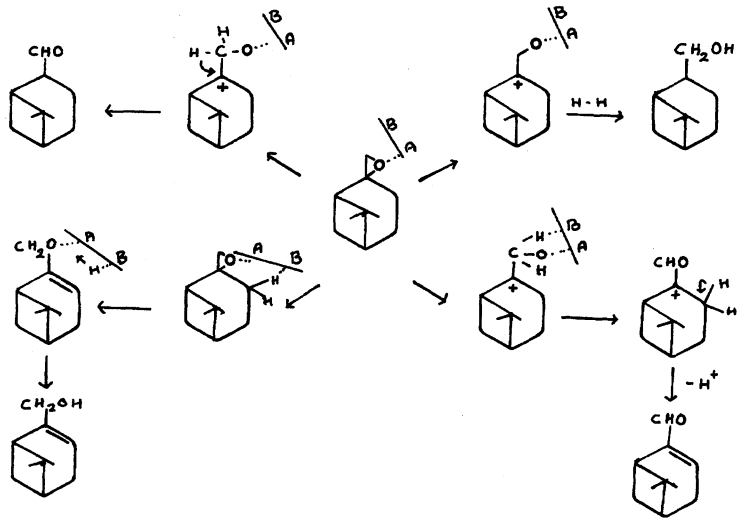


Chart 2.



Scheme 2.

Table 4. The Selectivity of Various Catalysts for the Isomerization of β-Pinene Oxide

Catalyst	Conversion	Selectivity/%				
	%	VI	X	XI	XII	XIII
Al_2O_3–Y_2O_3[a]	63	15	4	45		7
Al_2O_3–Sm_2O_3[a]	68	24	1	40	6	5
Al_2O_3–Eu_2O_3[a]	63	15	3	51	5	3
Al_2O_3–Nd_2O_3[a]	68	24	2	37	5	6
Al_2O_3–Pr_6O_{11}[a]	59	17		38	3	4
Al_2O_3–Y_2O_3[b]	50	6	6	10		8
Al_2O_3–Sm_2O_3[b]	63	14		5	7	5
Al_2O_3–Eu_2O_3[b]	56	29		5	9	6
Al_2O_3–Nd_2O_3[b]	53	32		4	8	6
Al_2O_3–Pr_6O_{11}[b]	57	24		5	5	5
Al_2O_3–Y_2O_3[c]	85	24		9	4	10
Al_2O_3–Sm_2O_3[c]	73	22		6	4	12
Al_2O_3–Eu_2O_3[c]	59	20		7	5	6
Al_2O_3–Nd_2O_3[c]	63	29		4	6	6
Al_2O_3–Pr_6O_{11}[c]	66	30		7	6	4

a) Reactions at 80 °C. b) Reactions at 110 °C. c) Reactions at 140 °C.

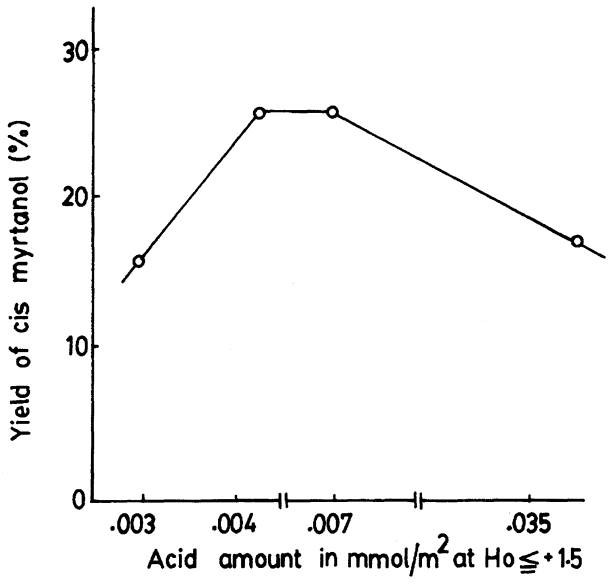


Fig. 4. Variation in the percentage yield of *cis*-myrtanol (**III**) with acid amount.

plays an important role in epoxide transformation. At 80 °C the percentage conversion of epoxide varied between 50 to 83% over different catalysts. Al_2O_3–Nd_2O_3 yielded maximum conversion of 83%. At 110 °C, total conversion ranged from 80 to 94%. Al_2O_3–Pr_6O_{11} produced a sharp increase in reaction rate at 110 °C, than that at 80 °C. At higher reaction temperature (140 °C), Al_2O_3–Eu_2O_3, and Al_2O_3–Nd_2O_3 produced complete transformation of epoxide to products. On other catalysts yield varied between 96 to 97%. When reaction rates of different catalysts were compared, Al_2O_3–Eu_2O_3 and Al_2O_3–Nd_2O_3 were found to be most suitable catalysts for α-pinene oxide isomerization.

Products in these reaction fall into four different categories viz. carbonyl compounds (**II**,**V**), allylic alcohol (**III**), saturated alcohol (**IV**, **VI**, **VII**), and diol (**VIII**). Carbonyl compounds were mainly produced in the reaction. Among carbonyl compounds 2,2,3-trimethyl-3-cyclopentene-1-acetaldehyde (**II**) is the major product formed. At 80 °C, Al_2O_3–Eu_2O_3 produced aldehyde (**II**) in 35% and the amount decreased to 31% at 110 °C. A further increase in amount of compound **II** was observed at 140 °C. Other catalysts yielded 2,2,3-trimethyl-3-cyclopentene-1-acetaldehyde in 29 to 40% at 80 °C. When reaction temperature increased to 110 °C, the yield of compound **II** varied in the range of 18 to 31% and it changed to the range of 18 to 46% at 140 °C. Lower temperature and higher acidity favour aldehyde formation and Al_2O_3–Eu_2O_3 was found to be the best catalyst system for the formation of **II**.

The formation of various products from α-pinene oxide is illustrated in Scheme 1. The epoxide oxygen attaches itself on an active centre on the catalyst surface. A carbonium ion is formed by the opening of epoxide bond which rearranges to various products.

It is well established that reaction of α-pinene oxide over Lewis acid catalysts like BF_3, $ZnBr_2$, HF yield carbonyl compounds.[7] The formation of major amounts of carbonyl compounds in our study clearly indicates Lewis acid sites on catalyst surface.

An attempt to correlate catalytic acidity and percentage production of aldehyde (**II**) was made and is given in Fig. 1. At 80 °C an increase in the yield of aldehyde (**II**) was observed with increase in acid amount at H_o values +3.3 and −3.

The formation of *trans*-pinocarveol (**III**) is less at 80 °C. At 110 °C the yield decreased with the exception of Al_2O_3–Sm_2O_3. At low reaction temperature, the percentage production of pinocarveol (**III**) varied between 11 and 17% and it changed to the range of 10 to 26% at 110 °C. At 140 °C, pinocarveol was produced in 10 to 22 % over various catalysts.

In the formation of *trans*-pinocarveol (**III**) basic sites on catalyst surface play an important role. Al_2O_3–Sm_2O_3 showed moderate acidity as well as basicity and was found to be best catalyst for the formation of **III**. With the exception of Al_2O_3–Sm_2O_3, other catalysts produced *trans*-pinocarveol (**III**) in smaller amounts than that of its saturated analogue (**IV**). Acid sites at $H_o \leqq +3.3$ and −3 seems to influence the formation of pinocarveol (**III**) at 110 and 140 °C. As evident from Fig. 2 an increase in yield of pinocarveol (**III**) is observed with increase in acid amount.

All catalysts except Al_2O_3–Pr_6O_{11} showed a reduction in the yielded of pinocamphol (**IV**) with rise in temperature. Compared to other products formed in the reaction, the reduction in the percentage yield of pinocamphol with rise in temperature is small. At 80 °C pinocamphol was produced in 14 to 21% over different catalysts and the yield changed between 17 to 21% at 110 °C. Al_2O_3–Y_2O_3 yielded 20% of pinocamphol (**IV**), at 110 °C and the amount decreased to 13% at 140 °C. At 140 °C other catalysts produced pinocamphol in 16 to 20%. Al_2O_3–Eu_2O_3 formed more pinocamphol at lower temperature. Al_2O_3–Nd_2O_3 was found to be the best catalyst for the production of pinocamphol (**IV**) at different temperatures.

Weak acid sites on catalyst surface seems to influence pinocamphol (**IV**) production. This is evident from Fig. 3. With increase in acid amount at $H_o \leqq +6.8$, +4, and +1.5 an increase in the percentage yield of pinocamphol was observed.

At 80 °C pinocarvone was produced in 15 to 25% yield by different catalysts. It is clear from Table 3 that the yield of pinocarvone is irregular with rise in temperature. Al_2O_3–Y_2O_3 produced 25% pinocarvone (**V**) at 80 °C and the catalyst showed a sharp reduction in the formation of **V** at higher temperature. At 110 °C the yield of pinocarvone varied from 4 to 19% and it increased to the range of 12 to 22% at 140 °C. It is evident from Table 3 that at 110 °C pinocarvone is formed in lesser amounts than that at 80 and 140 °C. In the case of pinocarvone (**V**) no increase in yield was observed with change in acid amount. Basic sites on catalyst surface play a role in pinocarvone production and Al_2O_3–Nd_2O_3 was observed to be best catalyst system at different temperature Besides these major products, some minor compounds like *cis*- and *trans*-myrtanol (**VI**,**VII**), pinene diol (**VIII**) were also formed in this transformation study.

Transformation of β-Pinene Oxide: β-Pinene oxide isomerized to give the following compounds as major products(Chart 2). *cis*- and *trans*-Myrtanal (**X** and **XI**), myrtenal (**XII**), *cis*-myrtanol (**VI**), and myrtenol (**XIII**).

The activity and selectivity of various catalysts are given in Table 4. The percentage conversion of epoxide varied from 59 to 68 at 80 °C and it decreased to the range of 50 to 63% at 110 °C. At 140 °C, an increase in percentage conversion of epoxide was observed. Over various catalysts at 80 °C carbonyl compounds were the major products formed in the reaction. At 110 and 140 °C alcohols are predominant.

As in the case of α-pinene oxide, the initial step is the formation of a tertiary carbonium ion by adsorption of an epoxide oxygen atom on catalyst surface. The carbonium ion rearranges to various products as given in Scheme 2.

The major product formed over various catalysts at 80 °C is *trans*-myrtanal (**XI**) and the yield varied from 37 to 51%. At 110 and 140 °C the formation of *trans*-myrtanal (**XI**) decreased. Al_2O_3–Eu_2O_3 produced 51% yield of *trans*-myrtanal while Al_2O_3–Y_2O_3 yielded 45%. A small increase in yield of *trans*-myrtanal (**XI**) was observed over various catalysts at 140 °C than that at 110 °C. *cis*-Myrtanal (**X**) was produced in smaller amounts of 1 to 4% at 80 °C. Except Al_2O_3–Y_2O_3, no other cat-

alysts produced *cis*-myrtanal (**X**) at 110 and 140 °C.

The yield of myrtanol (**VI**) varied from 15 to 24% over various catalysts at 80 °C. When reaction temperature increased to 110 °C, Al_2O_3–Eu_2O_3 produced an increase in yield from 15 to 29%. Compared to other products in the reaction, the yield of myrtanol (**VI**) is significant at all reaction temperatures and an overall increase is observed with rise in temperature. Myrtanol (**VI**) was produced in 20 to 30% yield at 140 °C. Comparing the transformations at three different temperatures 80, 110, and 140 °C, Al_2O_3–Nd_2O_3 was found to be best catalyst for myrtanol formation. In Fig. 4 the variation in the percentage yield of myrtanol with acid amount at $H_o \leqq +1.5$ is illustrated. With increase in acid amount percentage production of myrtanol increased. All catalysts except Al_2O_3–Y_2O_3, produced myrtenal (**XII**) in 3 to 6% yield at 80 °C and a slight increase in yield from 5 to 9% was observed at 110 °C. No myrtenal formation was observed over Al_2O_3–Y_2O_3 at 110 °C. Myrtenal was formed in 4 to 6% at 140 °C over various catalysts.

Along with other products myrtenol (**XIII**) is produced in minor amounts of 3 to 7% at 80 °C. When reaction temperature increased to 110 and 140 °C, increase in yield of myrtenol was insignificant. Al_2O_3–Y_2O_3 yielded 7 to 10% myrtenol at different temperatures. In the case of myrtenol and myrtenol there was no increase in the percentage production with increase in acidity.

Conclusion

Alunina-rare earth oxide catalysts had shown high potential in the catalytic transformations of epoxides. α-pinene oxide showed more reactivity than β-pinene oxide. 2,2,3-trimethyl cyclopentene-1-acetaldehyde (**II**), the major product obtained from α-pinene oxide has perfumery value. trans-Myrtanal (**XI**) the main product obtained from the reaction of β-pinene oxide at 80 °C is an established perfumery compound.

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