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ISOMERIZATION OF 1-METHYLCYCLOHEXENE OXIDE OVER SOLID ACIDS AND BASES

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The isomerization was carried out over metal oxides, sulfates and perchlorates in toluene at 108°C, and the selectivities were found to be strikingly different. SiO_2-Al_2O_3, solid H_3PO_4 and $LiClO_4$ formed almost 100% ketone, while TiO_2 and Al_2O_3 gave more than 80% allyl alcohol. Only $NiSO_4$ produced both products.

Not much work has been reported on the isomerization of epoxides catalyzed by solid acids and bases, although some work has been done recently on the isomerizations of propylene oxide[1] and ethylethylene oxide.[2] In the present work, we examined the extent, as well as the selectivity, of the reaction of 1-methylcyclohexene oxide over several solid acid and base catalysts.

The reaction was carried out in the presence of toluene as a solvent at 108°C for 2 hr. A mixture of 0.5 ml of the epoxide, 2.5 ml of toluene, and about 0.4 g of the catalyst less than 100 mesh was stirred in a reaction tube by a magnetic stirrer. The reaction products separated from the catalyst were analyzed by gas chromatography with a column of polyethylene glycol 20 M on Celite 545 SK.

TiO_2 and TiO_2-ZrO_2 (molar ratio = 1:1) were prepared by thermal decomposition of H_4TiO_4 and H_4TiO_4-$Zr(OH)_4$ in air at 500°C for 3 hr. The H_4TiO_4 and H_4TiO_4-$Zr(OH)_4$ were precipitated by adding aqueous ammonia to an aqueous solution of $TiCl_4$ and a mixed aqueous solution of $TiCl_4$ and $ZrOCl_2$ and washed thoroughly to remove adherent chloride ion. Al_2O_3 was KAT 6 of Nishio Chemical Co. and SiO_2-Al_2O_3 was N631(L) (Al_2O_3;15%) supplied by Nikki Chemical Co. Both catalysts were calcined in air at 500°C for 3 hr. The solid phosphoric acid was N501 of Nikki Chemical Co. and calcined in air at 300°C for 3 hr. $NiSO_4$ was prepared by calcining its heptahydrate in air at 350°C for 3 hr. MgO was prepared by calcining $Mg(OH)_2$ at 550°C for 3 hr. $LiClO_4$ and $NaClO_4$ were dried at 120°C for 3 days. Anhydrous $AlCl_3$ was a guaranteed reagent. 1-methylcyclohexene oxide, supplied by Takasago Perfumery Co., was fractionally distilled to purify to more than 98%.

Table 1 shows the % conversion of the isomerization and the % yield of the products. 2-Methylcyclohexanone (III) was predominantly formed over SiO_2-Al_2O_3, solid H_3PO_4, $LiClO_4$, and $AlCl_3$, while methylenecyclohexane-2-ol (VI) was predominantly given by TiO_2, TiO_2-ZrO_2 and Al_2O_3. In particular, the selectivity of SiO_2-Al_2O_3 for the formation of the ketone was 100%, but the selectivity of TiO_2 for the

formation of the allyl alcohol was 91%. Only $NiSO_4$ gave both products in the same ratio.

The activity of SiO_2-Al_2O_3, which has the highest acid strength, was comparatively low. Al_2O_3, which is one of typical Lewis acid catalysts, showed almost the same activity as that of solid H_3PO_4 (Brönsted acid). On the other hand, MgO, which has a basic character,[3] was almost inactive. The selectivity of $AlCl_3$ (Lewis acid) was similar to that of solid H_3PO_4. TiO_2-ZrO_2, which has a similar acidic property[4] to SiO_2-Al_2O_3, showed a different selectivity from SiO_2-Al_2O_3. These results seem to indicate that the activity and selectivity do not directly depend on the acidic or basic nature of the catalysts. In this point, it is interesting that $LiClO_4$ is highly active for the formation of ketone, though $NaClO_4$ is not so active.

Table 1 Catalytic activity and selectivity for isomerization of 1-methylcyclohexene oxide

Catalysts	Catalyst amount, g	Conversion, %	Products (%)[a] I	II	III	IV	V	VI
TiO_2	0.435	27.3		0.2	2.0		0.2	24.9
TiO_2-ZrO_2	0.298	92.1		2.6	4.2	9.1	10.2	65.2
Al_2O_3	0.340	90.4	trace	2.4	5.6	4.8	2.4	74.6
SiO_2-Al_2O_3[b]	0.473	42.3			42.3			
Solid H_3PO_4	0.370	87.7		1.2	86.5			
$NiSO_4$	0.360	89.4		3.3	43.4			40.9
MgO	0.238	2.3		1.3	0.9			
$LiClO_4$	0.290	87.3	0.5	0.3	86.5			
$NaClO_4$	0.656	8.4		0.6	5.5			2.3
$AlCl_3$[c]	0.50	95.5	1.4	1.0	79.6	1.7	3.1	1.9

a The products are as follows: I, 1-methylcyclohexene, II, unidentified, III, 2-methylcyclohexanone, IV, 1-methylcyclohexanol, V, 2-methyl-2-cyclohexene-1-one, VI, allyl alcohol (2-methylene-cyclohexanol and 2-methyl-2-cyclohexene-1-ol).

b A mixture of 1 ml of the epoxide and 5 ml of toluene was reacted at 100°C.

c The reaction was carried out at room temperature for 15 min.

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