Epoxide Rearrangement. VIII. The Acidic and Basic Properties of TiO_2-SiO_2-MgO and Its Catalytic Activities

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Four kinds of TiO_2–SiO_2–MgO having different molar ratios, TiO_2–SiO_2–MgO (1: 1: 1, 10: 10: 1, 1: 10: 10, and 10: 1: 10), were prepared, their acidic and basic properties being examined by titration with butylamine and benzoic acid in benzene, respectively. The acidity of TiO_2–SiO_2–MgO was attributed to that of TiO_2–SiO_2 and SiO_2–MgO. The amount of strong acid sites of $H_0 \leq -5.6$ decreased with the addition of MgO to TiO_2–SiO_2. The basicity of TiO_2–SiO_2–MgO was attributed to that of TiO_2–MgO and decreased with the increase in SiO_2 content. Catalytic activities for the isomerization of 1-butene and the decomposition of 4-hydroxy-4-methyl-2-pentanone are correlated with the acidity and basicity, respectively. For isomerization of 1-methylcyclohexene oxide and *d*-limonene oxide, TiO_2–SiO_2–MgO and TiO_2–SiO_2 showed high activities for the preferential formation of ketones except TiO_2–SiO_2–MgO (10: 1: 10) over which allyl alcohols were produced preferentially. The selectivities for the isomerization of two epoxides were interpreted in terms of the acidic and basic properties of the catalysts.

Binary metal oxides such as SiO_2–Al_2O_3,[2] TiO_2–Al_2O_3,[3] TiO_2–ZrO_2,[3] TiO_2–SiO_2,[4] SiO_2–MgO,[2,5] and TiO_2–MgO[6] have been investigated on acidic and basic properties and on their catalytic actions. Among the binary metal oxides, TiO_2–SiO_2 showed the highest acidic property; the acidity and acid strength of TiO_2–SiO_2 of a certain composition were found to be higher than those of SiO_2–Al_2O_3.[4] SiO_2–MgO is known to possess acid and base sites of moderate strength on the surface.[2,5] Recently, TiO_2–MgO has been found to show higher basicity than each component oxide. Thus, a mixed material of these three metal oxides, TiO_2–SiO_2–MgO, is expected to have both acid and base sites, the amount and strength of which may depend on the ratio of the three components.

No systematic investigation concerning both acidic and basic properties of multicomponent metal oxides except binary metal oxides has been performed, though many multicomponent metal oxides are often used as solid catalysts for many reactions. We have attempted to examine acidic and basic properties of TiO_2–SiO_2–MgO having different molar ratios and their relations to the catalytic actions for the isomerization of 1-butene, the decomposition of 4-hydroxy-4-methyl-2-pentanone and the isomerization of 1-methylcyclohexene oxide and *d*-limonene oxide.

Experimental

Catalyst Preparation. TiO_2–SiO_2–MgO with various compositions were prepared by kneading TiO_2–SiO_2 having different molar ratios of Ti to Si and magnesium hydroxide with a proper amount of water for 2 h, followed by drying at 120 °C for a day. TiO_2–SiO_2 was prepared by co-precipitation from a mixed solution of ethyl orthosilicate and titanium tetrachloride with aqueous ammonia.[4] The precipitate was aged over a water bath for 1 h, washed with distilled water until no chloride ion was detected and dried at 100 °C for a day. Magnesium hydroxide was prepared by the hydrolysis of magnesium chloride, followed by washing and drying as above.

All the catalysts were calcined in air at 500 °C for 3 h prior to reactions or measurements of surface properties.

Surface Area and X-Ray Analysis. A specific surface area was determined by applying the BET equation to the adsorption isotherm of nitrogen at −196 °C. X-Ray powder diffraction diagrams were recorded over the range of $2\theta = 20$—70° with an X-ray diffractometer (Toshiba ADG-301) by using nickel filtered Cu $K\alpha$ radiation.

Measurement of Acidic and Basic Properties. Acidity and basicity of catalysts at various strengths were measured by titrating with butylamine and benzoic acid in benzene, respectively, indicators of different pK_a's and pK_{BH} being used.[7,8]

Reaction Procedure. Isomerization reaction of 1-butene was carried out in a closed circulation system having a volume of about 900 ml at 200 °C.[4] 50 mg of a catalyst was placed in a reactor and evacuated at 200 °C for 2 h. The reactant (200Torr) was introduced and the products were analyzed periodically by gas chromatography. The analysis was carried out at 0 °C on a 4 m column containing 30 wt % propylene carbonate on Uniport C.

Decomposition of 4-hydroxy-4-methyl-2-pentanone to acetone was carried out at 30 °C for 10 min.[9] A mixture of 25 ml of 4-hydroxyl-4-methyl-2-pentanone and 0.5 g of a catalyst was stirred in a reaction vessel with a magnetic stirrer. For the analysis of products, a column packed with 10 wt% polyethylene glycol on chromsorb W and thermostated at 0 °C was used.

Isomerization of 1-methylcyclohexene oxide was carried out in the presence of toluene as a solvent at 108 °C for 2 h.[10] A mixture of 0.5 ml of the epoxide, 2.5 ml of toluene and about 0.3 g of a catalyst was stirred in a reaction vessel. The products were analyzed by gas chromatography, a 3 m column of polyethylene glycol 20M on Celite 545SK being used at 150 °C. For separation of two allyl alcohols, a 45 m capillary column of Ucon LB-500-X was used at 100 °C.

The procedure of reaction and analysis of products for the isomerization of *d*-limonene oxide[11] were similar to those for the isomerization of 1-methylcyclohexene oxide, except that a mixture of 1 ml of the epoxide and 5 ml of toluene was used.

Results and Discussion

Surface Area and X-Ray Analysis. Specific surface areas of catalysts are listed in Table 1. The values of

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* Part VII; see Ref. 1

Table 1. Specific surface areas of catalysts

	TiO_2	SiO_2	MgO	TiO_2–SiO_2			TiO_2–SiO_2–MgO			
Mole ratio				(1: 1)	(10: 1)	(1: 10)	(1: 1: 1)	(10: 10: 1)	(10: 1: 10)	(1: 10: 10)
Surface area ($m^2 g^{-1}$)	85	227	145	358	227	201	181	299	222	168

Table 2. Acidity at various acid strengths of catalysts

Catalysts	Mole ratio	Acidity (μmol m^{-2})				
		$H_0 \leqq +3.3$	$H_0 \leqq +1.5$	$H_0 \leqq -3.0$	$H_0 \leqq -5.6$	$H_0 \leqq -8.2$
MgO[a]			0	0	0	0
TiO_2–MgO[a]	(1: 2)	0	0	0	0	0
TiO_2–SiO_2	(1: 1)	1.6	1.4	0.6	*[b]	*[b]
	(10: 1)	2.7	3.5	0.1	*[b]	*[b]
	(1: 10)	2.2	0.9	0.8	0.3	0
TiO_2–SiO_2–MgO	(1: 1: 1)	3.6	2.8	2.5	1.5	0.4
	(10: 10: 1)	2.1	1.9	1.7	1.0	0.8
	(10: 1: 10)	1.9	1.6	0	0	0
	(1: 10: 10)	1.6	1.3	0.5	0.3	0

a) Cited from Ref. 6. b) See text.

mixed oxides were larger than those of single component oxide except SiO_2.

According to X-ray diffraction pattern, TiO_2–SiO_2–MgO (1: 1: 1 and 10: 10: 1) were amorphous and TiO_2–SiO_2–MgO (1: 10: 10 and 10: 1: 10) showed only weak diffraction lines of TiO_2 (anatase) and MgO. Since no diffraction lines of the hydroxides were detected, calcination in air at 500 °C is considered to cause the dehydration to form TiO_2–SiO_2–MgO.

Acidic and Basic Properties. Acidity at various acid strengths of TiO_2–SiO_2–MgO calcined at 500 °C is given in Table 2, together with that of TiO_2–SiO_2 and TiO_2–MgO. The acidity at $H_0 \leqq -5.6$ and -8.2 of TiO_2–SiO_2 (10: 1 and 1: 1) could not be determined by the titration method, since the color of the acidic forms of indicators of $pK_a \leqq -5.6$ and -8.2 is yellow and that of the above mentioned TiO_2–SiO_2 is of the same tone. However, it was confirmed that TiO_2–SiO_2 (10: 1 and 1: 1) has high acidity at $H_0 = -5.6$ and -8.2 from experimental results which showed that larger amounts of basic molecules (ammonia, butylamine, and pyridine) remain after evacuation at high temperatures on TiO_2–SiO_2 than SiO_2–Al_2O_3 which shows high acidity at $H_0 \leqq -5.6$ and -8.2.[4)]

The distribution of acidity on TiO_2–SiO_2 (1: 1) and TiO_2–SiO_2–MgO (10: 10: 1 and 1: 1: 1) indicates that the acidity at lower acid strength of $-3.0 < H_0 \leqq +3.3$ increases with an increase in the Mg content. This is considered to be due to the acidity of SiO_2–MgO resulting from the mixing of MgO with TiO_2–SiO_2 (1: 1). On the other hand, the acidity at $-3.0 < H_0 \leqq +3.3$ of TiO_2–SiO_2 (10: 1) decreases with the addition of MgO. This may be attributed to the fact that TiO_2–MgO which has no acidity occupies the main part in TiO_2–SiO_2–MgO (10: 1: 10). Similarly, the acidity of TiO_2–SiO_2–MgO (1: 10: 10) might be explained in terms of the acidic characters of SiO_2–MgO and TiO_2–SiO_2. The acidity at higher acid strengths of $H_0 \leqq -5.6$ and -8.2 of TiO_2–SiO_2 (1: 1 and 10: 1) decreases with the addition of MgO. In all TiO_2–SiO_2–MgO systems, only TiO_2–SiO_2–MgO (10: 1: 10) showed no acidity at $H_0 \leqq -3.0$.

Table 3. Basicity and catalytic activity for decomposition of 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol) at 30 °C

Catalysts	Mole ratio	Basicity[a)] (μmol m^{-2})	Activity[b)] ($\times 10^2$% m^{-2} min^{-1})
TiO_2–SiO_2	(1: 1)	0	—
TiO_2–MgO[c)]	(1: 2)	19.4	3.9
	(5: 1)	0	0
	(1: 18)	51.6	8.2
TiO_2–SiO_2–MgO	(1: 1: 1)	1.5	0.5
	(10: 10: 1)	0	0
	(10: 1: 10)	1.6	1.0
	(1: 10: 10)	2.0	1.8

a) 2,4-Dinitroaniline ($pK_{BH} = 15.0$) was used as an indicator. b) Mole percentage of the product at 10 min of a reaction time per unit surface area of catalyst (m^{-2}) per unit time (min^{-1}). c) Cited from Ref. 6.

The basicity of TiO_2–SiO_2–MgO and TiO_2–MgO calcined at 500 °C is given in Table 3. The high basicity of TiO_2–MgO (1: 2 and 1: 18) greatly decreased with the addition of SiO_2, TiO_2–SiO_2–MgO (10: 10: 1) showing no basicity.

Isomerization of 1-Butene. The activity and selectivity (the ratio of *cis-* to *trans*-2-butene) of TiO_2–SiO_2–MgO, TiO_2–SiO_2, and MgO for the isomerization of 1-butene are given in Table 4. The active sites of TiO_2–SiO_2 for the reaction were ascribed to acid sites. In the reaction, the *cis-/trans-* ratios were 1—2 and the reaction proceeds *via* a butyl cation.[4)] The ratio over TiO_2 was reported to be 4.2, suggesting a base-catalyzed isomerization *via* a π-allyl carbanion intermediate.[4)] The ratios over TiO_2–SiO_2–MgO (1.7—2.1) indicate that the same acid-catalyzed isomerization as over TiO_2–SiO_2 takes place, the activity being correlated with acidity (see Table 2) and not basicity.

Table 4. Catalytic activity and selectivity (ratio of *cis*- to *trans*-2-butene) for isomerization of 1-butene at 200 °C

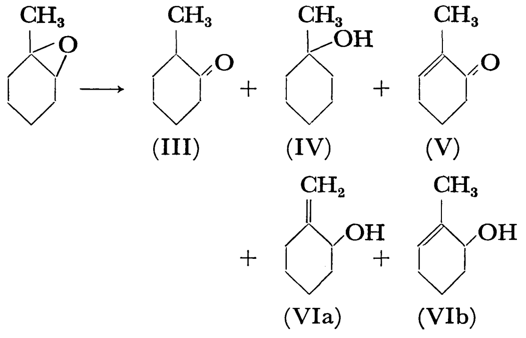
Catalysts	Mole raiio	Activity[a] ($\times 10^2$% m^{-2} min^{-1})	Selectivity[b]
MgO		0	—
TiO_2–SiO_2	(1: 1)	2.6	1.9
	(10: 1)	15.5	1.6
	(1: 10)	3.1	1.2
TiO_2–SiO_2–MgO	(1: 1: 1)	3.5	1.9
	(10: 10: 1)	2.9	1.9
	(10: 1: 10)	0.4	2.1
	(1: 10: 10)	1.1	1.7

a) Initial conversion per unit surface area of catalyst (m^{-2}) per unit time (min^{-1}).

b) Obtained by extrapolation to zero conversion.

Decomposition of 4-Hydroxy-4-methyl-2-pentanone. Catalytic activity as well as basicity of the catalysts are given in Table 3. A good correlation was observed between activity and basicity. Although TiO_2–SiO_2–MgO had acidic sites, the activity was small as compared with that of TiO_2–MgO which has no acidic sites. Thus, it is suggested that only basic sites are considered to be operative, and that the reaction proceeds as in the case of other solid base catalysts.[9]

Isomerization of 1-Methylcyclohexene Oxide. The reaction of 1-methylcyclohexene oxide over TiO_2–SiO_2–MgO, TiO_2–SiO_2, TiO_2, SiO_2, and MgO gave five main products: 2-methyl-cyclohexanone (III), 1-methylcyclohexanol (IV), 2-methyl-2-cyclohexene-1-one (V), 2-methylenecyclohexanol (VIa), and 2-methyl-2-cyclohexene-1-ol (VIb), with a small amount of 1-methylcyclohexene (I) and unidentified compound (II).



The activity and selectivity of catalysts in 2 h at 108 °C are shown in Table 5. The activity of three TiO_2–SiO_2 was higher than that of single component oxides. This fact is interpreted by taking into consideration the higher acidity of the former. It is of interest that TiO_2 formed the allyl alcohol (VI), but TiO_2–SiO_2 formed the ketone (III). Since formation of the ketone and the allyl alcohol is explained by isomerization over strong acid sites and acid-base bifunctional sites, respectively,[10] it is considered that comparatively weak acid sites and base sites exist on TiO_2 and strong acid sites exist on TiO_2–SiO_2.

Over TiO_2–SiO_2–MgO (1: 1: 1, 10: 10: 1, and 1: 10: 10), a high activity for the preferential formation of the ketone was observed. Although some basic sites were observed on TiO_2–SiO_2–MgO (1: 1: 1 and 1: 10: 10), they do not seem to be active. Only strong acid sites of $H_0 \leqq -3.0$ seem to be active. On the other hand, TiO_2–SiO_2–MgO (10: 1: 10) showed high activity and selectivity for the formation of the allyl alcohol. This suggests that TiO_2–SiO_2–MgO (10: 1: 10) has both base and acid sites at the proper acid strength to act as acid-base bifunctional sites; TiO_2–SiO_2–MgO (10: 1: 10) showed no acidity at higher acid strength of $H_0 \leqq -3.0$ (see Table 2).

Isomerization of d*-Limonene Oxide.* Isomerization of *d*-limonene oxide over the present catalysts gave the following products: cymene (II), 1-methyl-3-isopro-

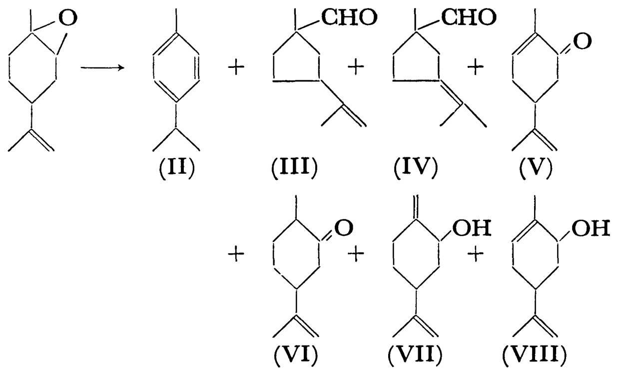


Table 5. Catalytic activity and selectivity for isomerization of 1-methylcyclohexene oxide at 108 °C at 2 h of a reaction time

Catalysts	Mole ratio	Amount of catalyst (g)	Conversion (%)	Products (%)[a]				
				(II)	(III)	(IV)	(V)	VI(a, b)
SiO_2		0.20	6	0	31	0	5	64
TiO_2[b]		0.44	27	0	7	0	1	91(51, 40)
MgO[b]		0.23	2					
TiO_2–SiO_2	(1:1)	0.27	34	11	80	6	1	0
	(9: 1)	0.28	47	21	45	6	2	12
	(1: 9)	0.31	46	9	57	7	1	3
TiO_2–SiO_2–MgO	(1: 1: 1)	0.32	54	0	64	15	1	2
	(10:10: 1)	0.29	45	6	61	12	1	2
	(10: 1: 10)	0.32	63	0	12	14	14	58(24, 34)
	(1: 10: 10)	0.22	46	2	61	7	3	5

a) See text. b) Cited from Ref. 10.

TABLE 6. CATALYTIC ACTIVITY AND SELECTIVITY FOR ISOMERIZATION OF *d*-LIMONENE OXIDE AT 108 °C

Catalysts	Mole ratio	Amount of Catalyst (g)	Conversion (%)	Products (%)[a]							
				(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
SiO_2[b]		0.16	1								
TiO_2[b]		0.32	25	0	0	0	0	0	6	58	25
MgO[b,d]		0.24	1								
TiO_2–SiO_2	(1: 1)[c]	0.26	100	7	2	18	3	4	48	0	0
	(9: 1)[c]	0.35	98	3	1	17	1	3	30	21	19
	(1: 9)[c]	0.28	98	2	1	15	2	5	41	8	14
TiO_2–SiO_2–MgO	(1: 1: 1)[c]	0.18	98	4	1	19	1	4	44	11	11
	(10: 10: 1)[c]	0.28	100	6	2	22	1	4	47	9	2
	(10: 1: 10)[b]	0.17	31	0	0	0	0	4	22	30	41
	(1: 10: 10)[b]	0.21	90	5	0	30	2	4	43	6	9
	(1: 10: 10)[c]	0.21	51	0	0	21	4	5	48	7	12

a) See text. b) Reaction time: 75 min. c) Reaction time: 10 min. d) Cited from Ref. 11.

penyl-1-cyclopentanecarbaldehyde (III), 1-methyl-3-isopropylidene-1-cyclopentanecarbaldehyde (IV), carvone (V), dihydrocarvone (VI), *exo*-carveol (VII), *endo*-carveol (VIII), and an unidentified compound (I).

The activity and selectivity of TiO_2–SiO_2–MgO, TiO_2–SiO_2, TiO_2, SiO_2, and MgO in 10 or 75 min at 108 °C are listed in Table 6. TiO_2–SiO_2–MgO (1: 1: 1, 10: 10: 1, and 1: 10: 10) and all TiO_2–SiO_2 showed surprisingly high activity for the ketone (VI) formation, as in the case of SiO_2–Al_2O_3 and $LiClO_4$.[11] TiO_2–SiO_2–MgO (10: 1: 10) was less active than any other mixed oxide, the allyl alcohols (VII and VIII) being preferentially produced. The selectivity for the reaction is similar to that for the isomerization of 1-methylcyclohexene oxide in the sense that the ketone was produced over acidic sites and the allyl alcohols over bifunctional sites. The selectivity in the isomerization of *d*-limonene oxide can be explained by the acidic and basic properties of the catalysts, as in the case of 1-methylcyclohexene oxide.

The products of II and IV were obtained in small amounts on the present catalysts, though large amounts were formed over SiO_2–Al_2O_3[11] which have strong acid sites of the Brönsted type. Thus, TiO_2–SiO_2–MgO and TiO_2–SiO_2 are considered to have no strong Brönsted acid sites.

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