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Epoxide Rearrangement III.[1] Isomerization of 1-Methylcyclohexene Oxide over TiO_2-ZrO_2, $NiSO_4$ and $FeSO_4$

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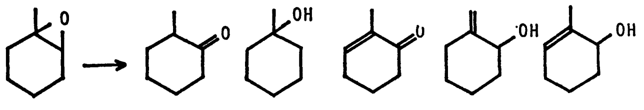
The reaction of 1-methylcyclohexene oxide at 108 °C was found to give predominantly 2-methylcyclohexanone (III) over $FeSO_4$, but predominantly allyl alcohols (VI) over TiO_2–ZrO_2 of various compositions. $NiSO_4$ gave the same amount of both products, III and VI. The selectivities over $FeSO_4$ and $NiSO_4$ were not much varied with calcination temperatures from 150 °C to 700 °C, while the catalytic activities were higher with $NiSO_4$ calcined at low temperature and with $FeSO_4$ calcined at high temperature. $FeSO_4$ and $NiSO_4$ gave the preferential formation of an allyl alcohol with *exo*-double bond, 2-methylene cyclohexanol (VIa), while TiO_2–ZrO_2 formed predominantly an allyl alcohol with *endo*-double bond, 2-methyl-2-cyclohexene-1-ol (VIb). Both the acidity and basicity of TiO_2–ZrO_2 were observed to increase by mixing each oxide and to correlate with the catalytic activity. The allyl alcohol formation was explained by an acid-base bifunctional mechanism.

We have recently reported some works on the isomerization of 1-methylcyclohexene oxide catalyzed by solid acids and bases,[1,2] where ketone (III) or allyl alcohols (VI) of five main products, with a small amount of 1-methylcyclohexene (I) and unidentified compound (II) (supposedly the dehydrated diene-compound of (VI)), was predominantly formed depending on the type of catalysts: $SiO_2 \cdot Al_2O_3$, H_2SO_4/SiO_2, low-temperature calcined solid H_3PO_4 and $LiClO_4$ produced almost 100% ketone, while Al_2O_3 and TiO_2 gave more than 80% of allyl alcohols (VI).[1]


III IV V VIa VIb

In connection with our interests in the strikingly different selectivities, we have examined further the catalytic properties of TiO_2–ZrO_2, $NiSO_4$, and $FeSO_4$ for this isomerization reaction from the following several points of view: 1) TiO_2–ZrO_2 showed much higher catalytic activity with the predominant formation of allyl alcohol than TiO_2,[2] and the existence of basic sites on the surface was suggested from the catalytic action for the partial conversion of ethanol into butadiene;[3] 2) $NiSO_4$ gave the same amount of both ketone and allyl alcohol[2]; and 3) $FeSO_4$ was found to show the significant catalytic activity for a preferential formation of ketone and also exhibited a surprisingly high catalytic activity for the Friedel-Crafts benzylation of toluene with benzyl chloride when calcined at high temperature.[4]

In the present paper, we discuss more in detail the catalytic activity and selectivity of TiO_2–ZrO_2, $NiSO_4$, and $FeSO_4$ for the isomerization of 1-methylcyclohexene oxide, particularly the relationship between the surface property and the selectivity.

Experimental

1-Methylcyclohexene oxide, supplied from Takasago Perfumery Co., was fractionally distilled to purify to more than 98% and toluene, a guaranteed reagent, used as a solvent was redistilled over sodium metal.

$NiSO_4$ and $FeSO_4$ were prepared by calcining their heptahydrates, guaranteed reagents of Wako Pure Chemical Co and Kanto Chemical Co., respectively. TiO_2, ZrO_2 and TiO_2–ZrO_2 of various compositions were prepared by thermal decomposition of H_4TiO_4, $Zr(OH)_4$ and H_4TiO_4–$Zr(OH)_4$, respectively. The procedure for the preparation of these materials was described previously.[3] All the catalysts were calcined in air and stored in sealed ampoules until use.

The procedures of reaction and analysis of the products were followed by those of the previous experiment.[1]

The amounts of base of TiO_2–ZrO_2 catalysts were measured by titrating the 100 mesh powder suspended in benzene with 0.1 M benzoic acid benzene solution, using 2,4,6-trinitroaniline ($pK_{BH}=12.2$) as an indicator.

Results and Discussion

The reaction of 1-methylcyclohexene oxide over TiO_2–ZrO_2, $NiSO_4$ and $FeSO_4$ catalysts gave five main products, 2-methylcyclohexanone (III), 1-methylcyclohexanol (IV), 2-methyl-2-cyclohexene-1-one (V), 2-methylenecyclohexanol (VIa) and 2-methyl-2-cyclohexene-1-ol (VIb), as observed in our previous paper.[1]

Table 1 shows the catalytic activities and selectivities of these catalysts in 2 hr at 108 °C. The over-all reaction followed first order reaction kinetics with respect to the oxide concentration except those with $NiSO_4$ calcined at 250 °C and $FeSO_4$ heat-treated above 400 °C, in which the reaction rate was found to diminish greatly after 30 min, probably owing to the contamination of the catalyst surface with some polymers produced by those high catalytic activities.

The products are mainly divided into two groups, ketone (III) and allyl alcohols (VI). The former was formed predominantly over $FeSO_4$, while the latter was given by TiO_2, TiO_2–ZrO_2 and ZrO_2 with a marked amount of IV and V, obviously formed by hydrogen transfers from V to IV (approximately the same yield found). $NiSO_4$ gave the same amount of both products. It is of interest that the selectivities are almost the same over $NiSO_4$ and $FeSO_4$ heat-treated at any temperatures from 150 to 700 °C, though solid H_3PO_4 formed almost 100% ketone when calcined at 200 to 300 °C, but gave the same amount of both

Table 1. Catalytic activity and selectivity of TiO_2-ZrO_2, $NiSO_4$ and $FeSO_4$ for isomerization of 1-methylcyclohexene oxide at 108 °C in 2 hr

Catalyst and calcination temperature, °C	Catalyst amount (A), g	Conversion (B) %	Activity $B\times\frac{0.3}{A}$	Yields (%)						
				I[a)]	II[b)]	III	IV	V	VI	(VIa, VIb)
TiO_2, 500	0.455	31.3	20.6		0.6	2.1			27.7	(15.1, 12.6)
TiO_2-ZrO_2[c)]										
3 : 1 500	0.393	83.0	63.3		0.9	6.5	1.5	1.6	72.5	(35.1, 37.4)
1 : 1 500	0.380	87.9	69.4		1.4	3.9	6.4	6.2	70.0	(28.1, 41.9)
1 : 1[d)] 500	0.298	92.1	92.7		2.6	4.2	9.1	10.2	65.2	(26.4, 38.8)
1 : 3 500	0.350	49.0	42.0		0.9	2.9	3.2	3.1	38.9	(15.1, 23.8)
1 : 3[d)] 500	0.290	52.8	54.6	0.6	0.8	3.5	3.7	4.7	38.9	(8.4, 30.5)
ZrO_2 500	0.329	3.3	3.0			0.7			2.6	
ZrO_2[e)] 350	0.321	24.5				4.0	4.1	3.0	13.4	(6.5, 6.9)
$NiSO_4$ 150	0.257	55.4	64.7	0.3	1.2	22.9		0.9	26.8	(19.1, 7.7)
250	0.390	75.8	58.3	0.5	11.0	47.6			10.3	(10.3, trace)
350	0.360	74.8	62.3			31.8			43.0	(35.7, 7.3)
400	0.324	34.4	31.9		0.3	12.9			18.4	(14.0, 4.4)
450	0.227	31.0	41.0	1.8	0.4	12.8			14.7	
500	0.210	17.8	25.4	trace	0.7	6.9			8.5	
600	0.250	13.3	16.0		0.5	5.8			6.7	(3.7, 3.0)
$FeSO_4$ 200	0.530	22.2	12.6			11.7			10.5	(7.6, 2.9)
300	0.315	65.9	62.7	4.0	3.8	40.9		0.8	11.4	
400	0.436	62.8	43.2	1.2	4.2	45.1		0.7	6.3	
500	0.339	72.2	63.9	3.9	2.4	56.3			4.3	
600	0.249	65.7	79.2		3.0	54.0			3.8	
700	0.166	37.8	68.3			24.4			12.3	(8.0, 4.3)

a) 1-Methylcyclohexene. b) Unidentified (supposedly dehydrated diene-compound of VI). c) Molar ratio. d) For those precipitated by ammonia following the method in Ref. 4. 4) Reaction carried out for 6 hr.

ketone and allyl alcohols when calcined at higher temperature, 400—900 °C, the formation of allyl alcohols being concluded to be due to the creation of basic sites on the surface at high temperature.[1)] This indicates that the active sites of $NiSO_4$ and $FeSO_4$ catalysts for this isomerization are not altered even if these catalysts were prepared at the high temperature such as 500, 600 or 700 °C, though the structural and catalytic changes caused by calcination temperature are known in both cases of $NiSO_4$[5)] and $FeSO_4$[6)]

The isomerization between ketone and allyl alcohols was not found in every reaction under the present reaction conditions. Heats of formation of allyl alcohols and ketone in gas phase at 25° were calculated by use of Benson *et al.*'s second-order approximation which is the law of additivity of group properties.[7)] They were −47.89 kcal/mol for 2-methylenecyclohexanol (VIa), −49.29 for 2-methyl-2-cyclohexene-1-ol (VIb) and −63.26 for 2-methylcyclohexanone (III). The differences in entropies of these materials were also calculated to be −1.94 e.u. for the entropy of ketonization of VIa to III, and +19.38 e.u. for that of VIb to III in gas phase at 25 °C. From these values, equilibrium constants of allyl alcohols to ketone were obtained to be 7.2×10^{10} for VIa to III and 3.6×10^{14} for VIb to III in gas phase at 25 °, indicating that the catalytic action of the present catalysts is quite selective.

An example of the time variation of the conversion to each product is shown in Fig. 1, where the catalyst is TiO_2–ZrO_2 (molar ratio=1 : 1). The reaction entirely followed first-order reaction kinetics with respect to the oxide concentration, and the conversions to III, IV, V, and VI increased almost parallel to each other with time. It is also seen that, in the formation of allyl alcohol, VIb exceeded VIa and isomerized gradually to VIa after 60 min. On the contrary, $NiSO_4$ (350 °C) gave much more VIa than VIb (Table 1), and the isomerization between them with reaction time was not observed: 12.0% (VIa) and 1.6% (VIb) at 30 min; 25.0 and 2.0 at 1.0 hr; 35.2 and 3.7 at 1.5 hr; and 35.7 and 7.3 at 2.0 hr. VIa generally exceeds VIb because

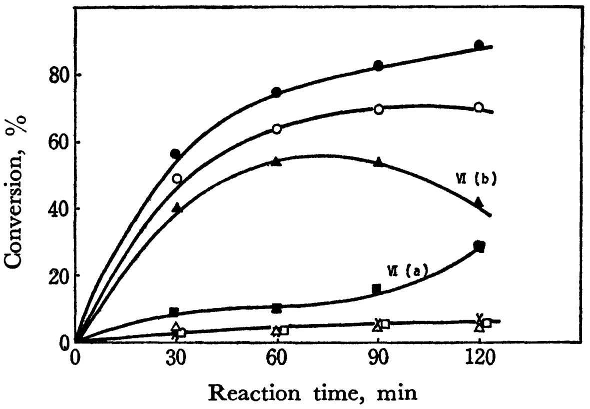
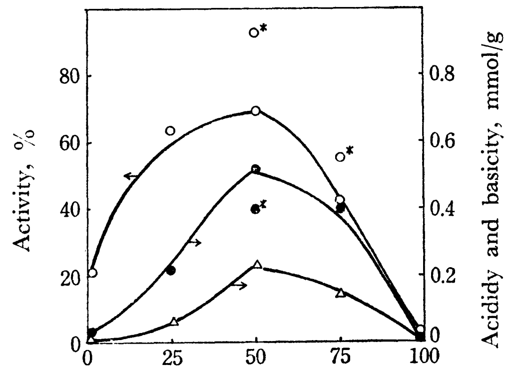


Fig. 1. Isomerization of 1-methylcyclohexene oxide over TiO_2-ZrO (1 : 1). (-●-) Total conversion, Conversion to III (-△-), IV (-×-), V (-□-), VI (-○-).

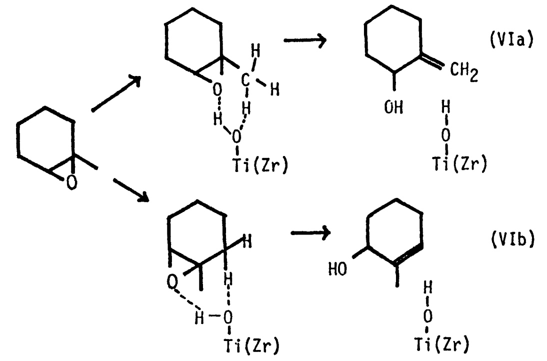


Molar ratio of $ZrO_2 : TiO_2$

Fig. 2. Catalytic activity, acidity and basicity of TiO_2-ZrO_2 at various compositions. (-○-) Activity, (-●-) Acidity[4] ($pK_a = -3.0$), (-△-) Basicity ($pK_a = 12.2$) : Basicity per surface area was 3.4×10^{-4} mmol/m^2, 9.0×10^{-4} and 7.3×10^{-4} for TiO_2-ZrO_2 (3 : 1), (1 : 1), and (1 : 3), respectively.[13]
* The sample precipitated by NH_3 following the procedure of Ref. 4.

of the preference of primary proton abstraction over secondary one caused by the more enhanced acidity of primary hydrogen by the electronic effect. Our previous observations followed this rule: 51.1% (VIa) and 23.5% (VIb) over Al_2O_3; 6.7 and 1.9 over zeolite H-F9; and 9.2 and 8.3 over solid H_3PO_4 heat-treated at 400°C.[1] The similar observations, the preferential formations of allyl alcohol with *exo*-double bond in the rearrangement of cycloalkene oxides, are found in literatures: for 1-methylcyclohexene,[8] 1-methylcycloheptene[8] and α-pinene oxides[9] with lithium diethylamide; for menthene and limonene oxides with aluminum isopropoxide[10]; and for limonene [11],α-pinene,[11,12] 1-methylcyclopentene[12] and 3-carene oxides with alumina.[12] The example opposite to the above rule, the favorable formation of allyl alcohol with *endo*-double bond, has not been found except for the case of 1-methylcyclopentene oxide with lithium diethylamide[8] and alumina,[12] probably caused by the stereochemically preferred geometry. As seen in Table 1, the TiO_2–ZrO_2 catalysts gave the preferential formation of VIb, while $NiSO_4$ and $FeSO_4$ formed predominantly VIa. Figure 2 shows the relation between catalytic activity and acidity as well as basicity of TiO_2–ZrO_2 at various compositions, where the total conversion % of the oxide per 0.3 g of the catalyst was taken as activity. TiO_2–ZrO_2 (1 : 1) changed 2,4,6-trinitroaniline ($pK_{BH} = 12.2$) to the basic color, but TiO_2 and ZrO_2 did not change the acidic color of BTB ($pK_a = 7.2$) to its basic color. It should be noted that both acidity and basicity increase by mixing TiO_2 and ZrO_2 up to the equal composition, as seen in the figure.

The catalytic activity correlates well with both the acidity and basicity. It is known that acid sites alone are active for the selective formation of ketone and basic sites alone are almost inactive for the isomerization of 1-methylcyclohexene oxide.[1] Therefore, these facts indicate that allyl alcohol, main product produced by the TiO_2–ZrO_2 catalysts, is formed on both acidic and basic sites on the catalyst. In other words, the allyl alcohol formation is explained by acid-base bifunctional mechanism. Since the acidic sites on the surface of TiO_2 prepared by calcining H_4TiO_4 in air are determined to be the Brönsted type,[15] the reaction is considered to proceed by the following mechanism.



An oxygen atom of the oxide adsorbs on a proton of the catalyst, while a hydrogen atom of the methyl or methylene group on oxygen (basic site) of the catalyst surface, and both the opening of the epoxide ring and the hydrogen abstraction from the methyl or methylene group take place simultaneously to form the allyl alcohol. The breaking of α-bond of oxygen is much more favorable due to the electronic effect of the methyl group, since no compound formed by the breaking of β-bond is found in the products. The choice of the VIa or VIb formation seems to depend on the distance between acidic and basic sites on the catalyst. The distance of TiO_2–ZrO_2 is supposed to be different from those of $NiSO_4$ and $FeSO_4$, judging from the preferential formation of VIb or VIa.

The acidic and basic strength of catalysts must be an important factor which controls the ketone formation. If the acid strength is too strong, the α-bond cleavage prior to the hydrogen abstraction would occur to form the ketone, while, if it is too weak, the hydrogen abstraction would hardly occur.

ZrO_2 calcined at 350 °C showed higher activity than that treated at 500 °C. The similar phenomena were also observed for the dehydration reaction of ethanol over ZrO_2, where the catalytic activity of the catalyst heat-treated at 400 °C was more than two times as high as that calcined at 500 or 600 °C.[4]

It is of interest that TiO_2–ZrO_2 (1 : 1 and 1 : 3) prepared by the coprecipitation method with NH_3 showed higher activity than those with urea, though the acidity was opposite to the activity. This seems to suggest the unusual surface property of TiO_2–ZrO_2.

Figure 3 shows the relation between catalytic activity and acidity of $NiSO_4$ and $FeSO_4$ calcined at various temperatures. The activity of $NiSO_4$ calcined at higher temperature correlates with its acidity measured by the indicator method. However, no correlation was found for $NiSO_4$ calcined at lower temperature. The high activity at low calcination temperature is considered to be due to the relatively weak Brönsted acid, which can not be measured by the indicator method, proposed by Ben-Dor and Margalith.[17]

In the case of $NiSO_4$ calcined at 250 °C, the conversion to VI was low compared to that for other

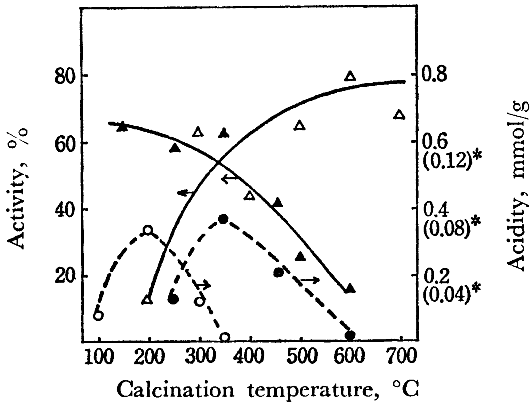


Fig. 3. Catalytic activity and acidity $(\mathrm{p}K_a=1.5)$[6,16] of $NiSO_4$ and $FeSO_4$ calcined at various temperatures. (▲) $NiSO_4$, (△) and (○) $FeSO_4$.
*Scale in parenthesis correspounds to $NiSO_4$.

$NiSO_4$ catalysts (Table 1). Since both the decrease of VI and the increase of II were observed during the course of reaction, it seems that VI was dehydrated to give II by strong Brönsted acid, because the maximum of Brönsted acidity of $NiSO_4$ appears when calcined at 250 °C.[18] It is inferred from the explanation about the reaction mechanism of the allyl alcohol formation as mentioned already that $NiSO_4$ has also basic sites because of the considerable formation of allyl alcohols.

The activity of $FeSO_4$ is not related to the acidity. Figure 3 shows that the higher the calcination temperature, the higher the catalytic activity. Since the preferential formation of ketone was concluded to be given by strong acid, it is supposed that additional acid sites, which were not observed by the butylamine titration method, were created when calcined at high temperature. However, the possibility that the active sites are different from acid sites can not be excluded in the case of $FeSO_4$.

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