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Isomerization of Cyclohexene Oxide over Solid Acids and Bases[1]

Kazushi ARATA and Kozo TANABE*,**
Hokkaido University of Education, Hachiman-cho, Hakodate 040
***Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060*

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The reaction of cyclohexene oxide over solid acids and bases at 108 °C gave five main products, 1,3-cyclohexadiene (**1**), cyclohexanone (**2**), cyclohexanol (**3**), 2-cyclohexen-1-one (**4**), and 2-cyclohexen-1-ol (**5**). SiO_2–TiO_2 and SiO_2–TiO_2–MgO were highly active for the isomerization, giving a large amount of **1**. TiO_2–ZrO_2 mainly showed selectivity for the formation of **5**, and other catalysts formed both **2** and **5**. Of the alumina prepared in four different ways, two were highly active, giving **5** predominantly. The results were discussed in comparison with those for an oxide containing a methyl group on the oxide ring, 1-methylcyclohexene oxide. By the experiment using the deuterated epoxide, 1,2-epoxycyclohexane-3,3,6,6-d_4, isotope effects for the formation of **2**, **3**, **4**, and **5** over Al_2O_3's, SiO_2–TiO_2 and solid H_3PO_4 were observed. It has been concluded that the epoxide is adsorbed on both acidic and basic sites, and that allyl alcohol is formed when both the opening of the epoxide ring and the hydrogen abstraction take place simultaneously, while ketone is formed when the former precedes the latter.

Studies on the rearrangement of cyclohexene oxide have been made. Nagvi and his coworkers reported for the first time that the oxide undergoes rearrangement in the presence of magnesium bromide etherate to *trans*-2-bromocyclohexanol and cyclopentanecarbaldehyde, a ring-contracted aldehyde.[2] The aldehyde formation from the oxide has been demonstrated using molten salts, low-melting binary or ternary eutectic salts as catalysts, *i.e.*, in the presence of lithium bromide or perchlorate with tributylphosphine oxide or hexamethylphosphoric triamide as reported by Rickborn and Gerkin,[3] or over lithium bromide–rubidium bromide eutectic supported on firebrick similar to the gas chromatography column reported by Kennedy and Buse.[4]

The isomerization of cyclohexene oxide to the uncontracted products has also been reported. Cyclohexanone was readily formed in alcoholic solutions of octacarbonyldicobalt(0),[5] 2-cyclohexenol being predominantly given by various lithium monoalkylamides and dialkylamides as strong bases.[6,7] The oxide was also converted into both cyclohexanone and 2-cyclohexenol by thermal gas-phase isomerization over the temperature range 407—464 °C under pressures 1.6—6 Torr (1 Torr=133.322 Pa).[8]

In contrast to the above observations on the homogeneous system, Al_2O_3 was used as a catalyst in the heterogeneous system.[9] However, diols or hydrated dimers were obtained instead of the isomerized products, probably owing to the incomplete dehydration of Al_2O_3 or adsorption of moisture caused by careless treatment.[10] Use of solid catalysts under heterogeneous conditions has the advantage of allowing easy separation of products from catalyst.

We have recently studied the isomerization of 1-methylcyclohexene oxide and *d*-limonene oxide catalyzed by solid acids and bases in a heterogeneous solid–liquid system, and observed the markedly different selectivities which depend on the type of catalyst.[11] Since only alumina has been investigated for the isomerization of cyclohexene oxide, the epoxide has now been isomerized over several solid acids and bases in order to see how the activity and selectivity differ according to the type of catalyst.

Experimental

Cyclohexene oxide (Tokyo Kasei Kogyo Co.) was more than 98% pure and toluene (guaranteed reagent) used as solvent was purified by distillation over sodium metal. 1,2-Epoxycyclohexane-3,3,6,6-d_4 (supplied by Dr. M. C. Flowers) was used. Purity of the epoxide was 99.5%, and isotopic purity was about 90% $C_6H_6D_4O$.

Standard Procedure for Reaction. The reaction was carried out at 108 °C in the presence of toluene as a solvent. A mixture of 0.5 ml of the epoxide, 2.5 ml of toluene, and about 0.3 g of catalyst, ground to below 100 mesh, was stirred in a reaction vessel with a magnetic stirrer. At appropriate time intervals, a small amount of the sample was taken out with a 1 ml syringe, separated from the catalyst by means of centrifuge, and analyzed by gas-liquid chromatography with a TCD detector using a 3-m column of 20% polyethylene glycol 20 M on Celite 545 SK (180 °C, He 1.0 kg/cm^2). The yields of products were based on the epoxide and calculated by measurement of GLC areas (uncorrected). The competitive isomerization of the deuterated and undeuterated cyclohexene oxide was carried out with a mixture of 0.1 ml of both oxides in equivalent amount, 0.5 ml of toluene and 60 mg of catalyst. The products were analyzed by combined gas chromatography-mass spectrometry (Hitachi RM50GC) with a 2-m column of PEG 20M.

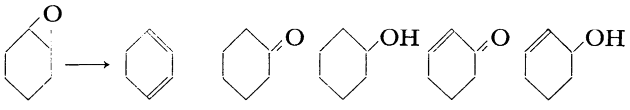
Catalysts. SiO_2–Al_2O_3 [N361(L)(Al_2O_3; 15 wt %) of Nikki Chemical Co.] was calcined at 500 °C. SiO_2–TiO_2 (molar ratio=1: 1) was prepared by coprecipitation of a mixed solution of ethyl orthosilicate and titanium tetrachloride with aqueous ammonia. The precipitate was aged over a water bath for 1 h, washed with distilled water until no chloride ion was detected, dried at 100 °C for 20 h and calcined at 500 °C. SiO_2–TiO_2–MgO (molar ratio=1: 1: 1) was prepared by kneading SiO_2–TiO_2 (1: 1) and magnesium hydroxide together with an appropriate amount of water for 2 h, followed by drying at 120 °C for 1 d and calcining at 500 °C. Magnesium hydroxide was prepared by hydrolysis of magnesium chloride with aqueous ammonia, followed by washing and drying as above. $LiClO_4 \cdot 3H_2O$ (guaranteed reagent, Nakarai Chemical Co.) was dried at 120 °C for 3 d. H_2SO_4/SiO_2 was prepared as follows: 10 g of granular silica gel was immersed in 12 ml of 0.5 M H_2SO_4, evaporated, dried and then calcined at 150 °C. $FeSO_4$ and $NiSO_4$ were prepared by calcining their heptahydrates (guaranteed) at 500 and 350 °C, respectively. Solid phosphoric acid (N501, Nikki Chemical Co.) was calcined at 300 °C. TiO_2–ZrO_2

(molar ratio=1: 1) was prepared by thermal decomposition, at 500 °C, of H_4TiO_4-$Zr(OH)_4$, which was precipitated by heating a mixed aqueous solution of titanium tetrachloride, zirconium dichloride oxide, and an excess amount of urea on a boiling water bath, followed by washing thoroughly with distilled water until no chloride ions were detected in the filtrate and drying in the air at 110 °C. Al_2O_3 A (KAT 6, Nishio Chemical Co.) was heat-treated at 500 °C. Al_2O_3 B, C, and D, Albes FF, Albes FE and Albes C, respectively, (Showa Tansan Kaisha, Ltd.) were calcined at 500 °C. All the catalysts were heat-treated in air for 3 h and stored in sealed ampoules.

Identification of Products. Reaction products were identified by the observed gas-chromatographic retention time and their mass spectra, obtained by combined gas chromatography-mass spectrometry, by comparison with authentic samples. A mixture of cyclohexene oxide (0.1 ml) and toluene (0.4 ml) was reacted over 60 mg of Al_2O_3 A at 110 °C for 2 h. The products were 5% of **1**, 2% of **2**, 6% of **3**, 30% of **5**, and 8% of **4** as the order of elution on a GLC PEG 20 M column at 180 °C. Their mass spectra at 70 eV of ionization voltage are as follows: important ions at *m/e* of **1**: 80 (M^+), 79 (100 %), 40 (78%), 80 (61%), 77 (36%), 78 (14%); **2**: 98 (M^+), 41 (100%), 55 (98%), 69 (82%), 42 (76%), 70 (35%); **3**: 100 (M^+), 57 (100%), 40 (51%), 82 (49%), 44 (38%), 67 (23%); **4**: 96 (M^+), 68 (100%), 40 (46%), 96 (42%), 39 (19%), 42 (10%); **5**: 98 (M^+), 70 (100%), 98 (50%), 97 (34%), 83 (30%), 39, (23%), 41 (22%).

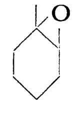
Results and Discussion

The reaction of cyclohexene oxide catalyzed by solid acids and bases gave 1,3-cyclohexadiene (**1**), cyclohexanone (**2**), cyclohexanol (**3**), 2-cyclohexen-1-one (**4**) 2-cyclohexen-1-ol (**5**), and other compounds.

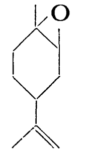


1 **2** **3** **4** **5**

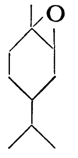
The products are substances expected from studies on the rearrangement of 1-methylcyclohexene oxide (A).[11a] Cyclopentanecarbaldehyde, a ring-contacted aldehyde, which was formed as the main product over molten salts or binary eutectic salts,[3,4] could not be detected, though the corresponding aldehydes were observed on the rearrangements of *d*-limonene (B) and carvomenthene oxides (C) over some of the present catalysts under the same reaction conditions.[11c,g]



(A)



(B)



(C)

The catalytic activity and selectivity of several solid acids and bases at 108 °C are given in Table 1. The catalysts were chosen on the basis of activity and selectivity for isomerization of 1-methylcyclohexene[11a,b] and carvomenthene oxides.[11g] The isomerization of 1-methylcyclohexene oxide was suggested to proceed *via* a carbonium ion intermediate.[2] Thus, cyclohexene oxide is considered to require a longer reaction time for the formation of secondary carbonium ions by cleavage of carbon–oxygen bond than 1-methylcyclohexene oxide which forms tertiary carbonium ions on carbon atoms bearing methyl groups. The results meet this expectation.

The time of reaction was so selected that appropriate conversion levels could be achieved. An example of

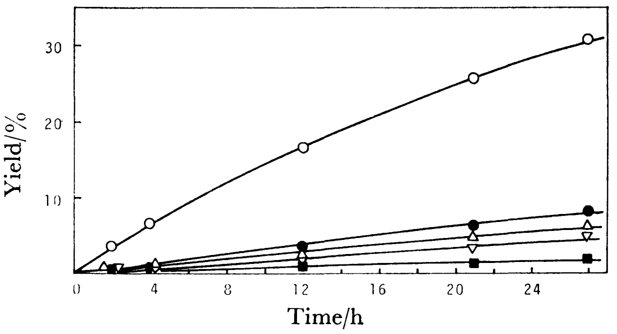


Fig. 1. Isomerization of cyclohexene oxide over TiO_2–ZrO_2 at 108 °C.
1 (△), **2** (■), **3** (▽), **4** (●), **5** (○).

TABLE 1. ISOMERIZATION OF CYCLOHEXENE OXIDE OVER VARIOUS SOLID ACID AND BASE CATALYSTS AT 108 °C

Catalyst	Catalyst amount	Reaction time	Total conversion	Product yields/%					
	g	h	%	**1**	**2**	**3**	**4**	**5**	others
SiO_2-Al_2O_3	0.36	12	29	2	7	1	2	6	12
H_2SO_4/SiO_2	0.26	24	6				1	0.5	5
$FeSO_4$	0.30	34	23	1	6		5	10	1
Solid H_3PO_4	0.41	21	28		7		4	15	1
$LiClO_4$	0.32	3	18	3	10				3
SiO_2-TiO_2	0.24	4	90	40	13	1	4	26	6
SiO_2-TiO_2-MgO	0.28	2	95	48	14	2	5	19	6
$NiSO_4$	0.42	48	11	1	5		1	4	
TiO_2-ZrO_2	0.32	27	51	6	2	5	7	31	
Al_2O_3 A	0.30	1	28	1	1	3	4	19	
Al_2O_3 B	0.18	2	30	1	3	3	6	16	1
Al_2O_3 C	0.39	12	29	2	8	1	10	7	1
Al_2O_3 D	0.20	4	39	3	10	1	8	16	1

time-variation of the products is shown in Fig. 1, where the catalyst is TiO_2–ZrO_2. The yields of all products increased almost parallel to each other during the course of reaction. A similar time-variation was observed for the other catalysts.

Cyclohexanol (**3**) was presumably formed by a hydrogen transfer from **4**, since the corresponding alcohol and α,β-unsaturated ketone were observed with approximately the same yield in the case of 1-methylcyclohexene oxide.[11b] **3** was formed with less yield in comparison with **4** in every case and at any time of reaction. **3** was probably converted into cyclohexene by its readsorption and dehydration on the catalyst surface during reaction periods. However, trace amount of cyclohexene was detected on GLC analysis. The olefin having a lower boiling point (82 °C) as compared with reaction temperature might have evaporated out of the reaction vessel.

In the case of 1-methylcyclohexene oxide, ketone was predominantly formed over SiO_2–Al_2O_3, H_2SO_4/SiO_2, $FeSO_4$, solid H_3PO_4, $LiClO_4$, SiO_2–TiO_2, and SiO_2–TiO_2–MgO, and allyl alcohol over TiO_2–ZrO_2 and Al_2O_3 A, the selectivities being more than 80% in both groups.[11a,b,f] $NiSO_4$ gave both products in the same amount. In the present work, the former catalysts produced unexpectedly large amounts of allyl alcohol, while the three latter catalysts, TiO_2–ZrO_2, Al_2O_3 A, and $NiSO_4$, showed catalytic actions analogous to the case of 1-methylcyclohexene oxide. Allyl alcohol formation is explained by an acid-base bifunctional mechanism.[11b] Strong acid sites are active for the selective formation of ketone,[11a] SiO_2–Al_2O_3,[12] SiO_2–TiO_2,[13] and SiO_2–TiO_2–MgO[11f] being known to have acid sites stronger than $pK_a = -8.2$ on their surfaces. In the present reaction, basic sites on these catalysts seem to play an important role. The slow reaction rate of the epoxide is due to the greater difficulty in formation of secondary carbonium ion intermediates on acid sites than that of the tertiary one for the case of 1-methylcyclohexene oxide. It is likely that the basic sites cause hydrogen abstraction during the course of cleavage of a carbon–oxygen bond by acid sites, even though the basic sites are weak.

In the case of *d*-limonene oxide,[11e] of the fibrillar aluminas Al_2O_3 B, C, and D, Al_2O_3 B predominantly formed allyl alcohols and Al_2O_3 D carbonyl compounds (ring-contracted aldehyde and ketone), both selectivities exceeding 75%, while Al_2O_3 C formed both products in the same amount. In the present case, however, Al_2O_3 D produced a considerable amount of allyl alcohol which can be understood by the above mechanism explaining the formation of allyl alcohol. The selectivities of Al_2O_3 B and C are comparatively close to those expected from the results on *d*-limonene oxide. Al_2O_3 A and B were extremely active for the present isomerization.

A large amount of diene **1** was formed over SiO_2–TiO_2 and SiO_2–TiO_2–MgO, and also in the isomerization of cyclohexene oxide catalyzed by solid acids and bases in gas phase, the diene formation being interpreted by the dehydration of 2-cyclohexen-1-ol.[11d] The results on cyclohexene oxide differ from those on 1-methylcyclohexene oxide. The difference might be caused by the easier readsorption of the present allyl alcohol on the catalyst surface to form the diene as compared with the case of the allyl alcohols formed from 1-methylcyclohexene oxide, because of the steric hindrance of the methyl group for readsorption of the hydroxyl group of the allyl alcohol. The interpretation leads to the observation of a smaller yield of **3** than that of **4**, *viz*., easy dehydration of **3** on the catalyst surface. The reaction of cyclohexene oxide seems to occur in the following series of parallel and consecutive steps,

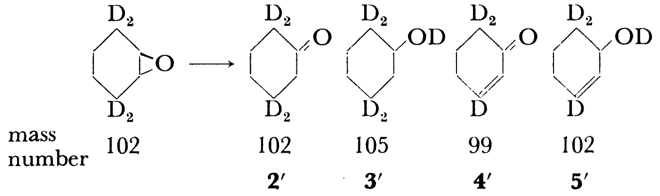
$$\begin{tikzcd}
 & \text{allyl alcohol} \arrow[r] & \text{diene} \\
\text{epoxide} \arrow[ur] \arrow[dr] & & \\
 & \text{ketone} &
\end{tikzcd}$$

In order to obtain further information on the reaction mechanism, the isomerization of cyclohexene oxide deuterated at the 3 and 6 positions, 1,2-epoxycyclohexane-3,3,6,6-d_4, was performed over Al_2O_3 A and the products were analyzed by combined gas chromatography-mass spectrometry. The product distribution and parent mass number of products are given in Table 2, the reaction scheme being as follows.

Table 2. Isomerization of 1,2-epoxycyclohexane-3,3,6,6-d_4 over Al_2O_3 A[a] and mass number of parent peak of products

Product	**2′**	**3′**	**4′**	**5′**
Yield/%	2	7	10	22
Mass number of parent peak	102	104	99	101

a) The reaction was carried out with 0.1 ml of the epoxide in toluene (0.4 ml) over the catalyst (60 mg) at 108 °C for 2 h. b) 2% of 1,3-cyclohexadiene was observed.



The mass numbers 104 and 101 shown for **3′** and **5′**, respectively, seem to be due to the alcoholic proton D^+ of **3′** and **5′** being exchanged with outer proton H^+ during the course of reaction and analysis. Al_2O_3 A consists of Lewis acid sites.[14] Thus, the exchange of proton between the epoxide and the catalyst surface could be excluded. **3′** and **4′** are considered to be formed by hydrogen (HD) transfers between two molecules of the oxide. Therefore, the above reaction scheme seems to be reasonable.

In order to obtain isotope effects for isomerization over catalysts, the competitive isomerization of deuterated and undeuterated cyclohexene oxide in equiamount was carried out over several catalysts, the products being analyzed by GLC-MS (Table 3). The d_0/d value was taken as the isotope effect for the isomerization of cyclohexene oxide. The primary isotope effect

TABLE 3. COMPETITIVE ISOMERIZATION OF 1,2-EPOXYCYCLOHEXANE AND 1,2-EPOXYCYCLOHEXANE-3,3,6,6-d_4 OVER SEVERAL SOLID ACID AND BASE CATALYSTS AT 108 °C FOR 1 h

Catalyst		Product			
		2	**3**	**4**	**5**
Al_2O_3 A	Yield/%	3	4	5	18
	d_0/d[a)]	4.7	1.2	4.1	2.1
Al_2O_3 D[b)]	Yield/%	3		1	2
	d_0/d	3.1		4.6	2.9
SiO_2–TiO_2	Yield/%	12			12
	d_0/d	2.8			3.1
Solid H_3PO_4[c)]	Yield/%	16			2
	d_0/d	1.7			

a) Relative intensity of parent peak between undeuterated and deuterated products. b) For 2 h. c) Heat-treated at 200 °C.

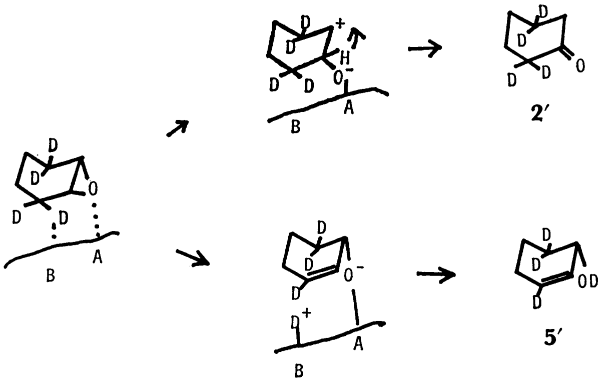
of the 3 or 6 position of cyclohexane ring can be seen for the formation of **2**, **4**, and **5**.

The allyl alcohol formation was interpreted in terms of the correlation between activity and acid-base property of catalyst by an acid-base bifunctional mechanism, where an oxygen of epoxide is adsorbed on an acidic site and a hydrogen atom of the methylene group on a basic site.[11)] The present isotope effect for **5** supports the reaction mechanism. The isotope effect for dehydration of isobutyl alcohol over Al_2O_3 by acid-base bifunctional mechanism determined to be 2.55 at 170 °C[15)] is close to our value.

Ketone formation, however, showed an unexpected primary isotope effect, indicating interaction between a hydrogen at the 3 or 6 position and a basic site on the catalyst surface. The formation of ketone is explained by the isomerization on strong acid sites in consideration of correlation between acid and base properties of catalyst and its selectivity.[11)] The cleavage of the oxygen bond takes place by adsorption of oxygen on a strong acid site with a subsequent shift of a hydrogen attached to a carbon atom bearing another oxygen bond. However, the isotope effect decreases in the order Al_2O_3 A, Al_2O_3 D, SiO_2–TiO_2, and solid H_3PO_4 with increase in the selectivity for ketone (Table 3). It can be concluded that ketone is formed selectively when acid sites play a more important role as compared with basic sites. In other words, a molecule of epoxide adsorbs on both an acid and a basic site, the extent of both adsorptions determining the selectivity. When both modes of adsorption are such that both the opening of the epoxide ring and the hydrogen abstraction take place simultaneously, allyl alcohol would be formed, while the cleavage of oxygen bond prior to the hydrogen abstraction would occur to form ketone if the acid is too strong.

Values of the isotope effect for **2** over Al_2O_3 A and D are comparatively large. These catalysts, especially Al_2O_3 A, probably affect the strong interaction between a hydrogen at the 3 or 6 position and a relatively strong basic site on the surface, together with the weak one between an oxygen and a weak acid site. Consequently, the anion formed on carbon would facilitate cleavage of the oxygen bond. However, this case seems to be limited, judging from the low yield of **2** on both aluminas. Since MgO and CaO catalysts, which have a stronger basic character than alumina, were inactive for the isomerization of 1-methylcyclohexene and *d*-limonene oxides,[11)] it seems that the oxide ring can not be opened by a basic site only without the effect of an acid site.

The reaction mechanism for the isomerization of cyclohexene oxide over solid acid and base catalysts is shown in the following.



The fact that the isotope effect for **4** is large but that for **3** is small seems to be reasonable in view of the deuterium distributions of products **3′** and **4′** which indicate the HD migration from a molecule of the oxide to another. The products of **3** and **4** were observed over the catalysts giving preferential formation of allyl alcohol. Thus, the intermediate species is considered to be related with the formation of both products.

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References

1) Epoxide Rearrangement XII. Part XI, see K. Arata J. O. Bledsoe, Jr., and K. Tanabe, *J. Org. Chem.*, **43**, 1660 (1978).

2) S. M. Nagvi, J. P. Horwitz, and R. Filler, *J. Am. Chem. Soc.*, **79**, 6283 (1957).

3) B. Rickborn and R. M. Gerkin, *J. Am. Chem. Soc.*, **90**, 4193 (1968); b) B. Rickborn and R. M. Gerkin, *ibid.*, **93**, 1693 (1971).

4) J. H. Kennedy and C. Buse, *J. Org. Chem.*, **36**, 3135 (1971).

5) J. L. Eisenmann, *J. Org. Chem.*, **27**, 2706 (1962).

6) J. K. Crandall and L. H. Chang, *J. Org. Chem.*, **32**, 435 (1967).

7) C. L. Kissel and B. Rickborn, *J. Org. Chem.*, **37**, 2061 (1972).

8) M. C. Flowers, D. E. Penny, and J. C. Pommelet, *Int. J. Chem. Kinet.*, **5**, 353 (1973).

9) V. S. Joshi, N. P. Damodaran, and S. Dev, *Tetrahedron*, **27**, 459 (1971).

10) K. Tanabe, "Solid Acids and Bases," Academic Press, New York/London (1970).

11) (a) K. Arata, S. Akutagawa, and K. Tanabe, *Bull. Chem. Soc. Jpn.*, **48**, 1097 (1975); (b) K. Arata, S. Akutagawa, and K. Tanabe, *ibid.*, **49**, 390 (1976); (c) K. Arata, S. Akutagawa and K. Tanabe *J. Catal.*, **41**, 173 (1976); (d) K. Arata, K. Kato, and K. Tanabe, *Bull. Chem. Soc. Jpn.*, **49**, 563 (1976); (e) K. Arata and K. Tanabe, *Chem. Lett.*, **1976**, 321; (f) T. Yamada, K. Arata, M. Itoh, H. Hattori, and K. Tanabe, *Bull. Chem. Soc. Jpn.*, **49**, 2946 (1976); (g) K. Arata, S. Akutagawa, and K. Tanabe, *ibid.*, **51**, 2289 (1978).

12) H. A. Benesi, *J. Phys. Chem.*, **61**, 970 (1957).

13) M. Itoh, H. Hattori, and K. Tanabe, *J. Catal.*, **35**, 225 (1974).

14) Ref. 10, p. 48.

15) H. Knözinger and A. Scheglila, *J. Catal.*, **17**, 252 (1970).