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Selective Synthesis of Dimethylamine (DMA) from Methanol and Ammonia over Zeolites

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The selective production of dimethylamine (DMA) from methanol and ammonia was studied over some zeolites and metal oxides at a temperature range of 300 ~ 450°C under ambient pressures. Proton or alkali-earth ion-exchanged zeolons were found to show considerable selectivity around 50% (product mole base) at 400°C. The selectivity for the sum of DMA and monomethylamine (MMA) which can be recycled again for DMA production was over 85% at the conversion level of 90%, indicating effective suppression of trimethylamine (TMA) formation over the zeolite. The selectivity is discussed in terms of the type, strength, and steric environment of the acidic active sites. The activation of ammonia, desorption of DMA, and the shape selective discrimination of the pore structure for TMA can be factors for the selectivity.

INTRODUCTION

High selectivity as well as activity of the zeolite catalysts have been recognized for some time (*1*). According to Venuto and Habib (*2*), its high selectivity for the gasoline production in the fluid-cracking catalyst (FCC) process which has brought about a revolution in petroleum refinery comes from the nature of its acidity and pore structure. Several shape-selective reactions have been reported characteristic for the zeolite catalysts (*3*). Above all, the recent innovation of gasoline synthesis from methanol over ZSM-5 is one of the most exciting catalyses by the zeolites, where a specified step in a series of consecutive reactions of methylene chain growth is most selectively and effectively terminated due to the molecular size limitation in the pore space (*4*), providing hydrocarbons of very restricted molecular weight range.

In the present study, a selective synthesis of DMA from methanol and ammonia was attempted over a variety of acidic oxides and zeolites. Such syntheses of methylamines and ethylamines over ZSM-5 and HZSM-5 (*5*) and catalytic aminations of alcohols, aldehydes, and ketones over some oxide catalysts (*6*) were reported, but both of activity and selectivity were still insufficient. Since the reaction of ammonia with methanol is consecutive, the certain step in a series of condensation should be terminated by prohibiting the further reaction of DMA to succeed the selective production of DMA. This kind of selectivity can be achieved by the acidic active sites, of which type or strength and location in the pore structure are adequately designed to prohibit the adsorption of DMA on the site or liberation of TMA from the pores. Prohibition of TMA liberation may force the amine to convert reversely to DMA.

EXPERIMENTAL

Materials. Commercially available methanol (Wako Junyaku Co.) and ammonia (99.99%, Seitetsu Kagaku Co.) were used without further purification. Zeolites and other catalysts as received forms are listed with their some characteristics in Table 1. The exchange with a tenth equivalent of aqueous ion at 80°C for 4 h was repeated three times. The ion-exchanged zeolites were dried at 100°C for 12 h. H^+-type zeolites, except for zeolon and ZSM-5, were prepared from ammonium ion-exchanged

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ones by calcining at 300°C for 6 h. Silica–magnesia was coprecipitated from the solution of colloidal silica and magnesium nitrate and calcined at 600°C for 3 h. All catalysts were screened to be of uniform size (35 ~ 48 mesh) after grinding.

Procedure. The reaction was performed in a flow reactor with a fixed catalyst bed. After ammonia was flown with helium carrier gas through the catalyst for 2 h to get a steady gas flow at the reaction temperature, methanol was charged by a microfeeder to start the reaction. The typical reaction conditions were: catalyst: 100 mg; ammonia, methanol: 0.07 atm; W/F: 4.8 min · mg_{cat}/ml. Methanol and the products were analyzed by occasional gas sampling at the tail of the reactor with a gas chromatograph (Yanako G180) using a glass column packed with Amipack 131 (3 m, Gasukuro Kogyo Co.). Except for reactions at 450°C, the activity of the catalyst was maintained for 6-h reaction in all runs within 90% of the initial activities. A good carbon balance and no coke formation was observed. At 450°C considerable coke formation was observed and the conversion decreased gradually to be about 60% value of initial one after 6-h reaction.

RESULTS

Product distributions and selectivities over various zeolites of as-received and H^+-exchanged forms are summarized in Tables 2 and 3, respectively, where the conversion, the yield and selectivity were calculated according to the following:

$$\text{conversion} = \frac{\text{moles methanol (inlet)} - \text{moles methanol (recovered)}}{\text{moles methanol inlet}} \times 100(\%) \quad (1)$$

$$\text{yield} = \frac{\text{moles of methanol in each product}}{\text{moles of methanol inlet}} \times 100(\%) \quad (2)$$

$$\text{selectivity} = \frac{\text{moles methanol in each product}}{\text{moles methanol (inlet)} - \text{moles methanol (recovered)}} \times 100(\%) \quad (3)$$

$$\begin{array}{c}\text{mole selectivity}\\ \text{(product mole base)}\end{array} = \frac{\text{mole product}}{\text{moles product detected}} \times 100(\%). \quad (4)$$

The dehydrocondensation reaction of methanol and ammonia into methylamines took place to a large variety of extents over the zeolites of as-received forms, the activities of the zeolite being classified into ZSM-5, Zeolon > 13X > Ω-5, E-5 > SK-40. Proton-exchanged zeolites exhibited much similar activities except for H^+-SK-45 and H^+-E-5.

The yield of DMA was normally lowest among those of methylamines over the zeolite catalysts examined in the present study except for the zeolon type. MMA and TMA were the major products at low and high conversion levels, respectively, suggesting difficulty in selective termination of the consecutive steps of the dehydrocondensation reaction over the zeolites other than zeolon catalysts.

In contrast, over the zeolon- of mordenite-type zeolite, DMA was the dominant product in spite of the high conversion around 86%, its mole selectivity being 38 and 42% over zeolons of as received and proton-exchanged forms, respectively. Since MMA could be converted to DMA by extending the contact time or recycling, sum of MMA and DMA can be a sensible

TABLE 1

Catalysts as Received Forms and Their Characteristics

Catalyst	Exchanged cation	Si/Al	Channel diameter (Å)	Number of oxygen in pore flame work	Dimension	Supplier
γ-Al_2O_3	—	—	—	—	—	Merck
H · A[a]	—	2	—	—	—	Shokubai Kasei
L · A[b]	—	5	—	—	—	Shokubai Kasei
SiO_2–MgO	—	(2)[c]	—	—	—	Prepared
HPC[d]	—	—	—	—	—	Climax Molybdenum
4A	Na	1	4.1	8	3	Shokubai Kasei
E-5	Na, K	3	3.6 × 5.2	8	3	Union Carbide
ZSM-5	H	24	5.2 × 5.8	10	2	Prepared
SK-45	Na	3	7.1	12	1	Union Carbide
Ω-5	Na, K	4	7.5	12	1	Union Carbide
Zeolon	H	5	6.7 × 7.0(3.9)[d]	12	1	Norton
13X	Na	1.5	7.4	12	3	Gasukuro Cogyo
SK-40	Na	2.5	7.4	12	3	Nikka Seiko

[a] Silica–alumina, high alumina (29 wt% Al).
[b] Silica–alumina, low alumina (14 wt% Al).
[c] Si/Mg.
[d] 12-Molibdophosphoric acid.
[e] Side pocket.

parameter for the catalyst evaluation. The mole selectivities for the sum over the zeolon catalysts exceeded 60%.

Activities and Selectivities of Zeolon Ion-Exchanged with Some Alkali, Alkali-Earth, and Transition-Metal Cations

Activities and selectivities of ion-exchanged zeolons for the methylation of ammonia at 400°C are summarized in Table 4. Except for the cupric ion-exchanged one, all zeolons examined showed excellent catalytic activities, giving the conversion higher than 75%. The conversion could exceed 90% over Mg and LaH zeolons at 400°C. DMA and (DMA + MMA) mole selectivities were also high on zeolon catalysts except for transition metal ion-exchanged ones, the selectivities exceeding 50 and 85%, respectively at the conversion level of 95% over LaH-zeolon. It may be significant that TMA produced was only 12% in the product slate at this conversion level. In contrast to alkali-earth ion or proton, the transition metal ion was failed to exhibit the selectivity for DMA, producing considerable amount of TMA. Thus, zeolons ion-exchanged by proper ions appear to exhibit significant selectivity for DMA by suppressing the production of TMA.

Some Conditions Influencing the Selectivity

The reaction temperature, partial pressures of the substrates, and the contact time may influence the catalytic reaction.

The catalytic activities and selectivities of some zeolons at variable temperatures are summarized in Table 4. The activity which was very low at 300°C was increased sharply at 350°C and reached a maximum at 400°C. The activity started to decrease at 450°C, probably because of the rapid catalytic deactivation by coke deposit. At lower temperatures, MMA was the dominant

TABLE 2

Catalytic Activities of Various Zeolites as Received Forms

Catalyst	Conv. (%)	Yield (%)[a]					Selectivity (%)			Selectivity (mol%)		
		MMA	DMA	TMA	DME	Others	DMA	MMA + DMA	TMA	DMA	MMA + DMA	TMA
E-5	43.2	10.8	16.9	14.3	0.8	0.3	39.1	64.2	33.2	34.3	78.3	19.4
ZSM-5	88.6	5.6	19.3	63.4	—	—	21.8	28.3	71.6	26.4	42.2	57.8
Ω-5	48.4	22.8	38.0	37.0	1.1	0.7	22.1	44.6	33.2	19.9	60.1	19.8
Zeolon	85.5	8.0	26.7	49.5	0.8	0.5	31.2	40.6	57.9	38.0	60.8	37.0
13X	72.7	4.5	9.0	55.7	1.9	0.9	12.5	18.8	77.1	16.0	32.3	62.6
SK-40	10.3	1.5	1.0	6.2	1.4	0.2	10.0	24.6	60.0	10.2	40.8	42.3

Note. Catalyst: 100 mg, reaction temp.: 400°C, W/F: 4.8 min · mg_{cat}/ml, P_{MeOH}, P_{NH_3} : 0.07 atm.

[a] MMA, monomethylamine; DMA, dimethylamine; TMA, trimethylamine; DME, dimethylether; others, ethylene, etc.

TABLE 3

Catalytic Activities of H^+-Exchanged Zeolites

Catalyst	Conv. (%)	Yield (%)					Selectivity (%)			Selectivity (mol%)		
		MMA	DMA	TMA	DME	Others	DMA	MMA + DMA	TMA	DMA	MMA + DMA	TMA
H^+-E-5	64.4	13.7	14.7	21.5	13.8	0.8	22.9	44.1	33.4	20.8	59.3	20.2
H^+-ZSM-5	86.5	7.6	21.2	56.7	1.0	0.1	24.5	33.3	65.5	28.1	48.5	50.1
H^+-SK-45	54.4	5.8	10.2	33.5	4.9	trace	18.7	29.3	61.6	20.7	44.3	45.6
H^+-Ω-5	70.8	10.7	15.2	44.4	0.6	—	21.4	36.5	62.7	22.8	54.8	44.4
H^+-Zeolon	86.0	15.9	38.2	31.0	0.9	—	44.4	62.9	36.1	41.8	76.4	22.6
H^+-SK-40	76.5	6.7	11.8	45.8	7.3	4.8	15.4	24.1	59.9	17.4	37.1	45.0

Note. Catalyst: 100 mg, reaction temp.: 400°C, W/F: 4.8 min · mg_{cat}/ml, P_{MeOH}, P_{NH_3}: 0.07 atm.

TABLE 4

Catalytic Activities of Metal-Ion-Exchanged Zeolon

M^{n+}	Temp. (°C)	Conv. (%)	Yield (%)					Selectivity (%)			Selectivity (mol%)		
			MMA	DMA	TMA	DME	Others	DMA	MMA + DMA	TMA	DMA	MMA + DMA	TMA
Na^+	300	19.5	9.3	4.4	3.6	2.2	—	22.5	70.0	18.4	16.1	83.3	8.7
	350	57.3	14.0	19.3	22.1	1.5	0.3	33.6	58.1	38.6	30.0	73.8	23.0
	400	85.5	9.1	30.4	44.5	0.9	0.6	35.6	46.3	52.0	38.0	61.3	37.0
	450	87.0	12.4	30.7	38.2	—	1.3	35.2	49.6	43.9	37.2	67.5	30.9
H^+	300	33.7	14.6	12.2	4.5	2.3	—	36.3	79.6	13.5	26.0	88.5	6.5
	350	69.0	22.1	29.4	15.5	2.0	—	42.6	74.7	22.5	34.0	85.5	12.0
	400	86.0	15.9	38.2	31.0	0.9	—	44.4	62.9	36.1	41.8	76.4	22.6
	450	72.2	12.4	12.3	16.7	7.4	9.3	17.0	34.2	23.2	19.0	57.5	17.3
Mg^{2+}	300	35.2	12.2	6.1	14.6	2.2	—	17.3	52.1	41.6	18.5	92.9	4.3
	350	81.5	22.0	43.6	15.3	0.6	—	53.5	80.5	18.8	44.3	89.0	10.4
	400	90.9	19.1	49.6	21.9	0.2	—	54.6	75.6	24.1	48.3	85.5	14.2
	450	74.8	19.8	18.1	18.4	—	5.0	24.3	50.8	24.7	24.2	77.0	16.4
$Mg^{2+}H^{+a}$	300	25.7	10.7	9.9	4.3	0.8	—	38.5	80.2	16.7	28.4	89.8	8.2
	350	53.4	15.7	26.7	10.5	0.5	—	50.0	79.4	19.7	40.8	88.8	10.7
	400	75.9	13.9	42.8	18.7	0.5	0.1	56.4	74.7	24.6	51.3	84.6	14.9
	450	64.5	11.2	16.6	11.2	1.9	9.5	41.3	43.0	17.5	28.7	67.2	13.0
$La^{3+}H^{+b}$	300	36.2	20.5	10.5	4.6	0.6	—	29.1	85.7	12.6	19.1	93.5	5.5
	350	81.3	25.0	35.6	20.0	0.6	0.1	43.8	74.6	24.6	35.7	85.9	13.4
	400	94.5	19.4	55.3	19.2	—	0.7	58.5	79.0	20.3	51.5	87.6	11.9
	450	78.2	13.8	21.7	17.9	—	6.1	27.7	45.3	23.0	32.1	73.2	17.8
Cu^{2+}	300	35.8	14.9	7.6	8.1	5.2	—	21.3	63.0	22.5	15.8	68.0	11.2
	350	71.3	13.0	10.5	42.6	5.2	—	14.7	33.0	59.8	14.9	52.0	40.5
	400	82.1	12.6	17.3	48.4	3.0	0.8	21.1	36.5	58.9	22.0	54.2	41.0
	450	70.8	13.8	15.6	19.0	2.4	5.8	22.1	41.5	26.9	24.4	67.4	19.8

Note. Catalyst 100 mg, W/F: 4.8 min · mg_{cat}/ml, P_{MeOH}, P_{NH_3}: 0.07 atm.

[a] 35% of H^+ was exchanged with Mg^{2+} ion.

[b] 50% of H^+ was exchanged with La^{3+} ion.

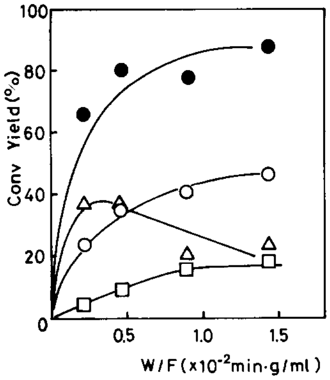


FIG. 1. The influences of contact time on product distribution over H-Zeolon. P_{NH_3}: 0.20 atm; P_{MeOH}: 0.07 atm; reaction temp., 350°C. ●, Conversion; △, yield of MMA; ○, yield of DMA; □, yield of TMA.

product at the low conversion level. The increasing conversion at higher temperature below 400°C increased the selectivity for DMA accompanied by the limited production of TMA, resulting in the rather selective production of the former amine. At 450°C MMA was again the dominant product at the reduced conversion.

High partial pressures of ammonia at the fixed partial pressure of methanol increased the selectivity for MMA, decreasing slightly that for DMA and sharply that for TMA. A partial pressure ratio of 3 (ammonia/methanol) appears most appropriate for the highest selectivity for DMA.

The influences of contact time are illustrated in Fig. 1, where the catalyst and the reaction temperatures used were H-zeolon and 350°C, respectively. The consecutive profile of DMA formation through MMA is clearly indicated. In contrast, the formation of TMA appears to level off around 15% of the yield at the relatively short contact time, increasing very slightly with the prolonged contact time.

Catalytic Activity of Some Oxides for the Formation of Methylamines

The catalytic activities of some acidic oxides for the formation of methylamines are summarized in Table 5, for the comparison against the zeolite catalysts. The alumina catalyst (a strong Lewis acid) showed an almost exclusive activity for dimethylether (DME), especially at lower reaction temperatures, in spite of the presence of ammonia. Increasing the reaction temperature till 400°C enhanced the formation of only DME. At 450°C, some amount of methylamines was produced, however, TMA was the dominant product. Silica–alumina, a strong Brönsted acid, showed very high activity for the formation of DME at 300°C. The increased reaction temperature sharply reduced the selectivity for DME to increase methylamines, TMA being always dominant among the methylamines.

Over silica–magnesia, a weak Brönsted acid which produced methylamines rather selectively even at 300°C, increased their yields with the increasing reaction temperature, however, TMA was always dominant among the methylamines. The mole selectivity for DMA was 30% at highest at restricted conversion levels under the present conditions.

DISCUSSION

The catalytic properties influencing the formation of methylamines, especially selectivity for DMA, may be the type and strength as well as sterical environment of the acidic active sites. The low activity of alumina for methylamines may exclude the Lewis acidity from the effective active sites. It is suggestive to compare the activities of silica–alumina and silica–magnesia, which are believed to have strong (<-8.2 in Ho) and medium ($-3 \sim 7$ in Ho) strength of Brönsted acidity, respectively (*7*). DME was almost exclusively produced over silica–alumina at lower reaction temperatures, suggesting that ammonia is too strongly adsorbed and stabilized on its strong acid sites to react with methanol, two molecules of which can be, instead, converted into the ether on the site of weakened acidity by ammonia. Higher reaction temperature is required to activate ammonia adsorbed on the strong acid site

TABLE 5

Catalytic Activities of Some Solid-Acid Catalysts

Catalyst	Temp. (°C)	Conv. (%)	Yield (%)					Selectivity (%)			Selectivity (mol%)		
			MMA	DMA	TMA	DME	Others	DMA	MMA + DMA	TMA	DMA	MMA + DMA	TMA
γ-Al_2O_3	300	23.9	—	—	—	23.9	—	—	—	—	—	—	—
	350	56.1	0.8	0.6	trace	54.6	—	1.1	2.6	trace	1.1	4.0	trace
	400	79.1	3.6	2.9	trace	72.5	—	3.7	8.3	trace	3.6	12.5	trace
	450	85.2	6.4	8.2	24.5	46.2	—	9.6	17.1	28.8	9.9	25.1	19.6
H.A.	300	72.7	3.3	3.3	—	66.1	—	4.5	9.0	—	4.2	12.9	—
	350	81.0	5.9	6.3	31.1	37.7	—	7.8	15.1	38.4	8.3	23.9	27.2
	400	90.4	8.6	13.2	63.9	4.3	—	14.6	24.4	70.7	16.9	39.7	54.6
	450	94.2	13.3	22.7	56.6	1.6	—	24.2	38.3	60.1	25.7	55.7	42.6
SiO_2–MgO	300	13.7	1.1	1.8	8.4	2.4	—	13.4	21.4	61.4	15.3	33.5	46.7
	350	42.0	1.9	2.8	33.0	4.2	trace	6.7	11.3	78.6	8.5	20.1	67.1
	400	66.0	2.4	7.6	54.1	2.0	0.3	11.5	15.1	81.6	15.0	24.4	71.2
	450	78.5	5.7	18.8	52.0	1.0	1.0	24.0	31.2	66.2	28.1	45.1	51.8

Note. Catalyst: 100 m, W/F: 4.8 min · mg_{cat}/ml: P_{MeOH}, P_{NH_3}: 0.07 atm.

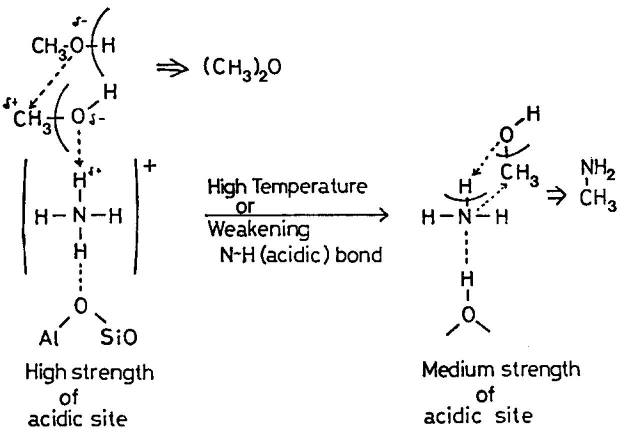


FIG. 2. A schematic explanation: the influences of the acid strength of the catalyst and the reaction temperature on the production of methylamines.

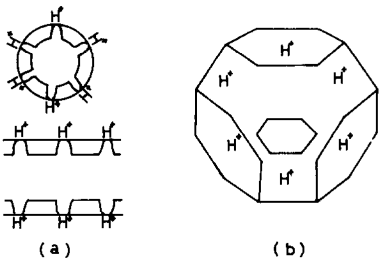
to be reactive with methanol into methylamines. In contrast to the strong acid site of silica–alumina, the acid sites of medium strength on silica–magnesia allow ammonia to react with methanol into methylamines at moderate reaction temperatures. Such correlations of selectivity for methylamines with acid strength and reaction temperature can be schematically illustrated in Fig. 2.

According to above discussion, the high selectivity of zeolite catalysts for methylamines can be ascribed to the moderate strength of their acidic sites. Proton-type zeolites have been reported to have acid-strength distribution ranging from 12 to 3 in Ho acidity function (*8*), however major sites are assumed to be of medium strength weaker than those of silica–alumina (*7*).

The selectivity for DMA in methylamines should be discussed based on the consecutive nature of the reaction as clearly illustrated in Fig. 1. The acid strength may influence the selectivity through the desorption of DMA and/or replacement with ammonia or MMA from the acidic sites. The acidic site of high strength may sustain the amines produced until the reaction is completed in the formation of TMA. The moderate strength is, thus, favorable for higher selectivity of DMA, allowing the competitive adsorption of ammonia and methylamines.

Sterical circumstances around the acidic site may influence the selectivity in two manners. The certain neighboring groups of the acidic site can weaken the adsorption of DMA through their repulsive steric interaction. Although such a selectivity may be expected to be associated with transition metal ions coordinated to the ligands (amines under the present conditions), no selective formation of DMA was achieved over the zeolon exchanged with the transition metal ions in the present study.

Other sterical circumstances are associated in a more macroscopic sense with the pore structure of the catalyst where the acidic sites are located. Such a selectivity has been well recognized with zeolite cata-



(a) (b)

FIG. 3. The pore structures of representative zeolites (see Ref. (9)). (a) Zeolon. (b) SK-40.

lysts by the name of shape-selective (*2*). The high selectivity of zeolons for DMA by hindering the formation of TMA may be explained in terms of their pore structure. The pore structure of zeolon, a synthetic mordenite, illustrated in Fig. 3a (*9*) is characterized by the pockets on the pore wall having a free diameter of 3.9 Å (*9*). TMA may not be allowed to be produced or liberated in the pocket (minimum molecular sizes (Å) estimated using HGS models (*10*) are: MMA: 2.2 ± 0.2, DMA: 3.0 ± 0.2, TMA: 3.9 ± 0.2), resulting in the selective termination of consecutive steps. In contrast, the pores of the faujasite zeolites have windows or large diameter (ca. 7 Å) to let TMA freely pass as illustrated with SK-40 (Y-zeolite) in Fig. 3b. The acidic sites, which are located on the wall of such pores, may not perform any discrimination against TMA.

In conclusion, the high selectivity of LaH-zeolon can be ascribed to the Brönsted acidity of the adequate strength located in the pockets, which can carry out the shape-selectivity through their inlet diameter.

REFERENCES

1. Venuto, P. B., and Landis, P. S., *Adv. Catal.* **18,** 259 (1968).

2. Venuto, P. B., and Habib, Jr., E. T., *in* "Fluid Catalytic Cracking with Zeolite Catalysts." Dekker, New York, 1979.

3. Chen, N. Y., Lacki, S. L., and Mower, E. B., *J. Catal.* **13,** 329 (1969); Frilette, V. J., Weisz, P. B., and Golden, R. L., *J. Catal.* **1,** 301 (1962); Weisz, P. B., Frilette, V. J., Mastman, P. W., and Mower, E. B., *J. Catal.* **1,** 307 (1962); Bryant, D. E., and Kranich, W. L., *J. Catal.* **8,** 8 (1967); Chen, N. Y., and Weisz, P. B., *Chem. Eng. Progr. Symp. Ser.* **63,** 86 (1967); Csicery, S. M., *J. Catal.* **19,** 118 (1970).

4. Meisel, S. L., McCullough, J. P., Lechthaler, C. H., and Weisz, P. B., *Chemtech* **6,** 86 (1976); Chang, C. D., and Silverstri, A. J., *J. Catal.* **47,** 249 (1977).

5. U.S. Patent 4,082,805 (1978).

6. Klyuev, M. V., and Khidekel', M. L., *Russ. Chem. Rev.* **49,** 14 (1980).

7. Benesi, H. A., *J. Phys. Chem.* **61,** 970 (1957); Tanabe, K., *in* "Metal Oxides and Compound Oxides" (Tanabe, K., Seiyama, T., and Fueki, K., Eds.), p. 291. Kodansha Scientific, Tokyo, 1978.

8. Otsuma, H., Arai, Y., and Ukihashi, H., *Bull. Chem. Soc. Jpn.* **42,** 2449 (1969).

9. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., *in* "Chemistry of Catalytic Processes," p. 57. McGraw–Hill Book, New York, 1979.

10. The model is distributed by Maruzen Co., Tokyo.