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Isomorphous Substitution in Zeolite Frameworks

II. Catalytic Properties of [B]ZSM-5

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The catalytic activity of [B]ZSM-5 is examined for a number of acid-catalyzed reactions: *n*-hexane cracking, xylene isomerization, ethylbenzene dealkylation, cyclopropane isomerization, and hydrocarbon formation from methanol. In each case, it was determined that catalytic activity was due mainly, if not entirely, to trace amounts (80–580 ppm) of framework Al. The remarkable effectiveness of minute concentrations of framework Al in ZSM-5 zeolites has had little recognition until recently.

INTRODUCTION

Zeolites whose silica frameworks contain substituents other than Al are found in nature (*1*). Such structures can also be prepared in the laboratory, either by crystallization (*1, 2*), or framework modification with various reagents (*3*). These substances are drawing increasing attention as catalysts with potentially unique properties. One of the more frequently mentioned in this regard, particularly in the recent patent literature, is [B]ZSM-5. Recent studies on [B]ZSM-5 using high-resolution ^{11}B MASNMR emphasize the ease of B incorporation into the ZSM-5 framework (*24*). Even Pyrex autoclaves used in synthesis proved to be sources of B (*24*). [B]ZSM-5 has been reported to catalyze the cracking and aromatization of olefins (*4–6*) and paraffins (*6*), propylene oligomerization (*25*), xylene isomerization (*7*), ethylbenzene dealkylation (*7*), and methanol conversion to hydrocarbons (*4, 8*). Methanol conversion to hydrocarbons over [B]ZSM-11 has also been reported (*23*). According to Taramasso *et al.* (*13*), [B]ZSM-5 catalyzes the alkylation of benzene with ethylene, but is "almost inactive" for methanol dehydration. The present study examines the activity of [B]ZSM-5 containing varying amounts of framework B for a selection of acid-catalyzed reactions: *n*-hexane cracking, xylene isomerization, ethylbenzene dealkylation, cyclopropane isomerization, and methanol conversion to hydrocarbons. The effect of alumina binders (*9*) on the activity of [B]ZSM-5 is also explored.

EXPERIMENTAL METHODS

Materials. [Al]ZSM-5 was synthesized by the method of Argauer and Landolt (*10*). [B]ZSM-5 was synthesized by an adaptation of the Argauer and Landolt method (*11*). Table 1 contains a list of zeolite samples prepared, along with their B and Al contents. Elemental analyses were done by atomic absorption spectroscopy. Boron analyses were supplemented by XRD lattice contraction measurements (*12*) and/or temperature-programmed NH_3 desorption (TPAD). Lattice contraction was shown by Taramasso *et al.* (*13*) to be a satisfactory indicator of tetrahedral B concentration in zeolite frameworks. The differential TPAD curve for [B]ZSM-5 shows a maximum at about 170°C (*14*). The supplemental tests

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TABLE I

Chemical and Catalytic Properties of [B,Al]ZSM-5

Sample	Boron, wt%			Aluminum (ppm)	n-Hexane cracking (α)	Ethylbenzene dealkylation, $k \times 100$ (hr^{-1})	Cyclopropane isomerization, k (sec^{-1})
	Elemental analysis	Lattice contraction	TPAD				
A	0.00	—	—	270	1.9	88	19
B	0.00	—	—	360	2.5	117	31
C	0.00	—	—	428	3.1	180	40
D	0.26	0.26	—	80	0.1	4.3	0.32
E	0.27	0.28	—	580	6.0	260	72
F[a]	0.37	0.49	—	337	1.2	112	17
G	0.42	0.49	0.42	320	1.7	106	21
H	0.54	—	0.50	280	2.1	89	17
I[a]	0.57	0.56	—	267	1.2	60	7
J	0.58	—	0.65	355	2.8	108	33
K	1.02	—	0.88	345	2.8	129	25

[a] 80% crystallinity.

confirm that the B is in the framework in these preparations. The zeolites were converted to the H-form by NH_4^+ exchange followed by calcination at 538°C (*15*).

Hydrocarbon reagents and methanol used were ACS reagent grade.

Apparatus and procedures. Catalytic reactions were carried out in fixed-bed, continuous-flow microreactors consisting of 8-mm-i.d. stainless-steel tubing, electrically heated, and each with an axial thermowell (3-mm o.d.). These reactors contained about 1 g of 14/30 mesh catalyst. Liquids were metered into the reactors by positive displacement pumps (ISCO, Inc., Lincoln, Nebr.), and gases through Brooks mass-flow controllers (Emerson Electric Co., Hatfield, Pa.). In the xylene isomerization and ethylbenzene dealkylation study, the microreactor as well as product sampling and analysis, and data acquisition, was automated. The system was controlled by HP 9830A, PDP11/44, and VAX 11/750 computers as schematized in Fig. 1. Products were analyzed by gas chromatography. n-Hexane cracking experiments were conducted using equipment and procedures described by Olson *et al.* (*15*).

EXPERIMENTAL RESULTS

n-Hexane cracking. The effect of framework B concentration on the n-hexane cracking activity of [B]ZSM-5 was evaluated at 538°C, using the α-test. The α activities observed varied from 0.1 to 6.0, and are listed in Table 1. These data are plotted against %B in Fig. 2A. A lack of correlation between n-hexane cracking activity and B concentration is apparent. However, when the data are replotted against Al concentration, a positive correlation is revealed, as shown in Fig. 2B. This is in general agreement with the results of Olson *et al.* (*15*), who found α to be proportional to framework Al content in ZSM-5. These data indi-

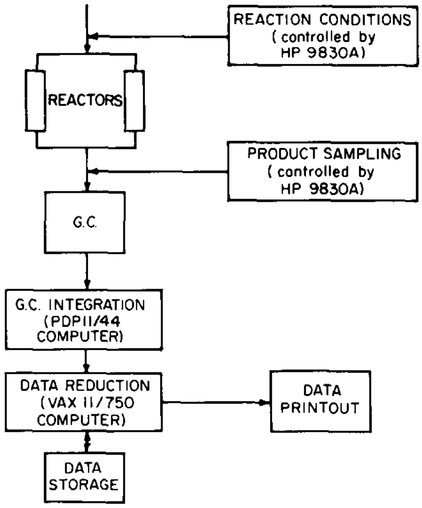


FIG. 1. Schematic diagram of automated microcreator system.

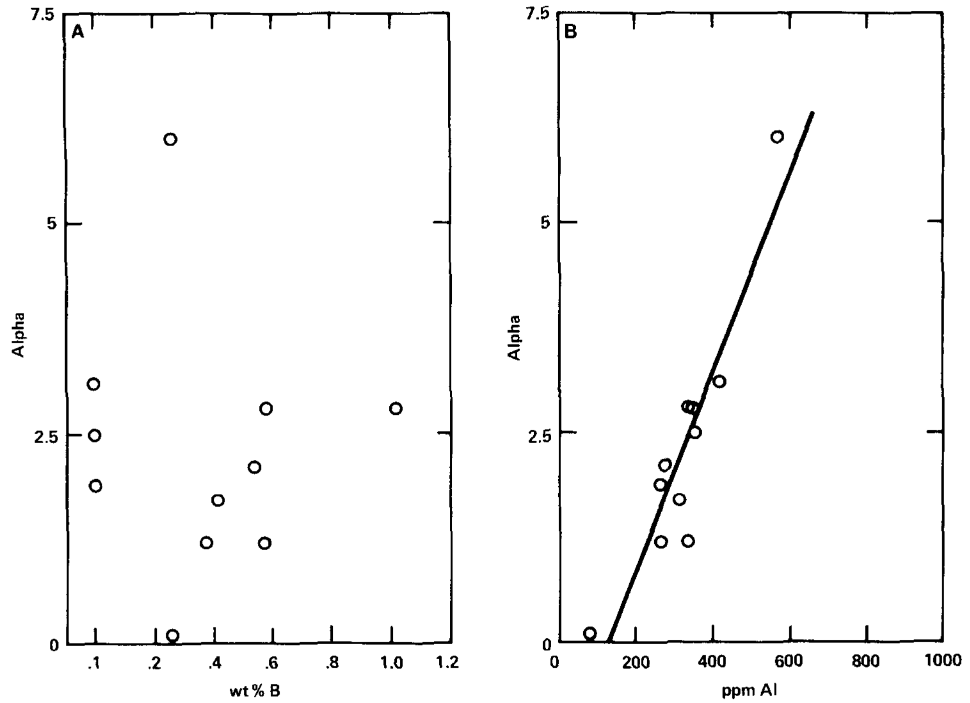


FIG. 2. (A) Effect of B content of α activities. (B) Effect of Al content on α activities.

cate that the B[OH]Si site in [B]ZSM-5 contributes little or nothing to the overall activity for paraffin cracking, and that observed activity may be accounted for solely by the small amount of Al present in the zeolite sample.

Xylene isomerization and ethylbenzene dealkylation. These two reactions were investigated simultaneously using a reactant mixture consisting of 80% *m*-xylene and 20% ethylbenzene, which simulates a commercial isomerization feedstock. Reactions were carried out at 427°C and 35 atm, in the presence of hydrogen (H_2- to-hydrocarbon mole ratio of 7). In the following discussion, the *p*-xylene "approach to equilibrium" is used to characterize reaction selectivity, and is defined by the expression

$$([p\text{–xyl}]_{\text{obs}}/[p\text{–xyl}]_{\text{eq}}) \times 100,$$

where the concentration [*p*–xyl] is normalized on a total xylenes basis. Experimental results are summarized in Table 2. Approach to equilibrium is plotted against

TABLE 2

Xylene Isomerization and Ethylbenzene Dealkylation

	Catalyst sample[a]											
	D			E			B			J		
WHSV, hr^{-1}	5.42	7.90	11.85	5.82	8.74	16.23	6.34	9.52	17.68	6.34	9.52	17.68
p-Xylene approach to equilibria %	6.80	3.80	3.67	101.35	99.09	91.91	96.43	87.45	79.80	110.28	87.63	81.33
EB conversion, %	0.63	0.20	0.22	33.84	26.47	18.05	15.99	12.76	8.14	15.94	10.29	6.77

Note. Feed: 80% *m*-xylene, 20% ethylbenzene (EB). Reaction conditions: 427°C, 10.2 atm, H_2/HC (mole ratio) = 6.5.
[a] See Table 1 for B and Al content.

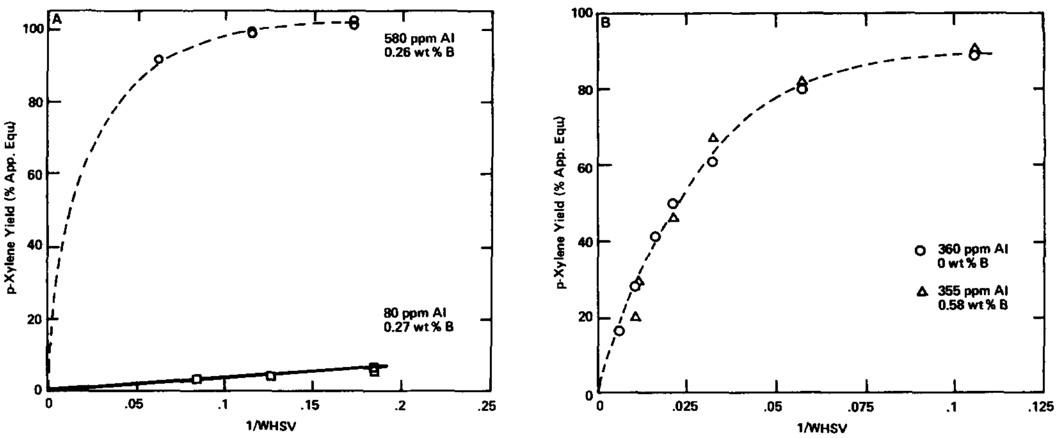


FIG. 3. (A) p-Xylene equilibrium vs WHSV^{-1}. Influence of Al. (B) p-Xylene equilibrium vs WHSV^{-1}. Influence of B.

reciprocal space velocity in Figs. 3A and B. In Fig. 3A the B concentration is held essentially constant at 0.26–0.27% while Al concentration is varied from 80 to 580 ppm. For comparison, the Al concentration in Fig. 3B is held at 355–360 ppm while a 0.58% B sample (Sample J) is compared against a B-free sample (Sample B). As evidenced in Fig. 3A, a substantial increase in activity results upon increasing the Al content from 80 to 580 ppm, with equilibrium quickly established in case of the higher Al catalyst. On the other hand, as seen in Fig. 3B, the activity of the 0.58% B sample is identical to that of the B-free sample at a fixed Al concentration. These data show that the observed activity of [B]ZSM-5 for xylene isomerization is due mainly, if not entirely, to Al in the zeolite samples.

Ethylbenzene dealkylation kinetics are pseudo-first order as indicated by the semilog plots in Fig. 4A, which are based on data from the B-free samples (Samples A, B, and C), and Fig. 4B, which shows two sets of data at constant %B (Samples D and E). Rate constants for ethylbenzene dealkylation for the entire set of catalysts are listed in Table 1 and plotted in Fig. 5 against Al content. A linear correlation results. In this plot, the open circles are data from the B-free samples (see also Fig. 4A), while the shaded circles represent the B-containing

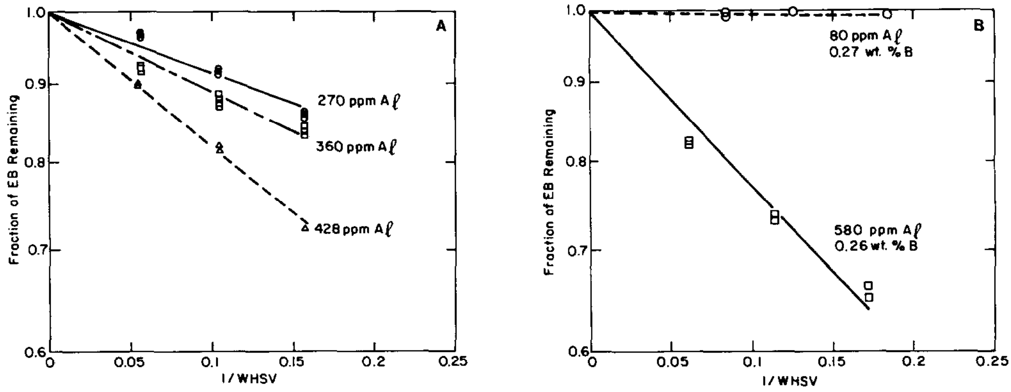


FIG. 4. (A) First-order semilog plots of ethylbenzene dealkylation. Effect of Al content (no boron). (B) First-order semilog plots of ethylbenzene dealkylation showing dominant effect of Al content. Ethylbenzene conversion also includes transalkylation and other secondary reactions.

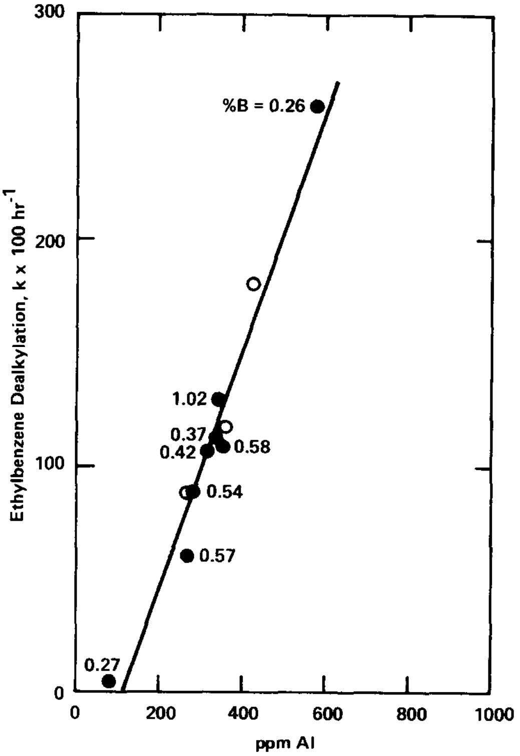


FIG. 5. First-order rate constants for ethylbenzene dealkylation as a function of Al content over a range of B content (wt% B indicated next to data points).

samples, with their B contents indicated. Again, a lack of correlation with B is evident.

Cyclopropane isomerization. This is a relatively facile reaction which is known to obey first-order kinetics in the presence of zeolite catalysts (*16, 17*). Cyclopropane was reacted over the set of catalysts A–K at 250°C, 1 atm, in the presence of a helium diluent ($He/cyC_3 = 4$). First-order rate constants are listed in Table 1 and plotted in Fig. 6 against Al concentration. As in the previous plot, the open circles represent B-free samples and the shaded circles the B-containing samples. As with the other reactions, cyclopropane isomerization correlates with Al but not B content.

Methanol conversion to hydrocarbons. The zeolite-catalyzed methanol conversion to hydrocarbons (*18–20*) has received considerable attention and is the basis of the Mobil process for gasoline synthesis from coal or natural gas. Methanol was reacted at 370°C, 1 atm, and 1 LHSV over catalyst Samples B (0% B, 360 ppm Al) and J (0.58% B, 355 ppm Al). Data listed in Table 3 show no significant effect of B on selectivity, however, the B-containing catalyst was actually less active than the B-free material. Both catalysts produced significant amounts of paraffins, which is symptomatic of coke laydown since no aromatics are formed.

Effect of alumina binder on xylene isomerization and ethylbenzene dealkylation. The catalytic experiments described above were all conducted using pure zeolite crystals. Zeolite-based catalysts in commercial applications are normally bound in a matrix such as alumina for mechanical strengthening. In the course of this study it was found

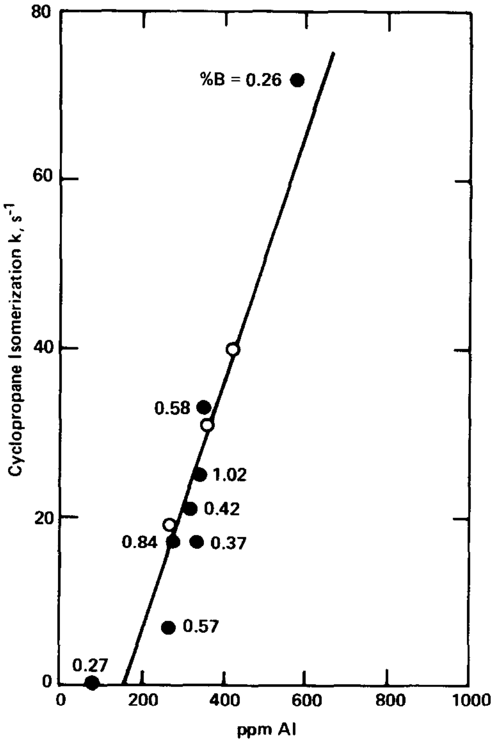


FIG. 6. First-order rate constants for cyclopropane isomerization as a function of Al content over a range of B content (wt% B indicated next to data points).

TABLE 3

Methanol Conversion to Hydrocarbons[a]

	Catalyst	
	B	J
B, wt%	0	0.58
Al, ppm	360	355
Conversion, % [CH_2]	36	21
Hydrocarbons, wt%		
Methane	0.9	1.7
Ethane	<0.1	0.4
Ethene	6.3	6.2
Propane	1.2	2.4
Propene	36.6	25.8
Butanes	9.6	14.3
Butenes	17.9	15.6
Pentanes	12.1	15.7
Pentenes	12.3	16.3
C_6^+ aliphatic	3.1	1.6
Aromatics	0	0

[a] 370°C; 1 atm; 1 LHSV.

that the catalytic activity of [B]ZSM-5 for xylene isomerization and ethylbenzene dealkylation was significantly enhanced when bound with alumina. A portion of Sample D (0.26% B, 80 ppm Al) was dispersed in a γ-alumina hydrosol, basified with NH_4OH, dried at 165°C, and calcined at 538°C. A commercial xylene isomerization feedstock was reacted over both the unbound and bound zeolite at 427°C, 6.3 WHSV, 10 atm, and with H_2 co-feed (H_2/m-xylene = 7). Results are summarized in Table 4, where the binder activation may be clearly seen. In a companion publication (*9*) the mechanism of this binder activation is shown to involve the transport and insertion of Al into the zeolite framework in tetrahedral coordination. It is further shown that Al substitution is facilitated by the presence of framework B because of the hydrolytic instability of B and hence its ready replacement.

DISCUSSION

Based on the above data it is clear that the acid activity of the B(OH)Si site is extremely low if at all existent. This contradicts the current literature on [B]ZSM-5 catalytic properties. Any activity due to the B(OH)Si site will be masked by the activity due to extremely small amounts of Al introduced during synthesis, when precautions are not exercised to exclude trace Al from reagents. This seems to have escaped the notice of other workers in the field. In the present study, only one sample (Sample D) was synthesized using silica gel which had been exhaustively extracted with HCl to reduce Al contamination, while other preparations used a commercial silica sol (Ludox), which contained small amounts of Al which varied from batch to batch. This is somewhat reminiscent of the question of the purported activity of silica gel for such reactions as double-bond isomerization (*26*), and t-butylbenzene dealkylation (*27*), which was ultimately traced to Al impurities. Double-bond isomerization is, however, an extremely facile reaction. t-Butylbenzene dealkylation is somewhat more demanding, requiring about 1800 ppm Al in

TABLE 4

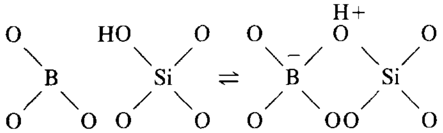
Binder Activation of [B]ZSM-5 for Xylene Isomerization and Ethylbenzene Dealkylation

	Feed	Catalyst	
		Sample D	D + Binder
Run No.		296	1–2
TOS (hr)		29	22
Products, wt%			
Paraffins	1.85	1.85	0.58
Benzene	—	—	0.12
Toluene	—	—	—
EB	19.99	19.88	19.61
p-Xylene	0.52	1.87	16.16
m-Xylene	52.86	51.12	41.59
o-Xylene	24.77	25.28	21.93
C_9 + aromatics	—	—	—
Normalized xylenes			
p-Xylene	0.66	2.39	20.28
m-Xylene	67.64	65.31	52.20
o-Xylene	31.70	32.30	27.50
p-Xylene, % equilibrium[a]	2.8	10.2	86.3
m-Xylene, % converted	—	3.3	21.3
% EB converted	—	0.5	1.9

[a] Xylenes equilibrium at 427°C: *p*-xylene 23.5, *m*-xylene 52.1, *o*-xylene 24.2.

silica gel for measurable conversion (*27*). In contrast, the Al content of the zeolites used in this study ranged from 80 to 580 ppm, corresponding to a minimum of 1 Al per 58 unit cells, and a maximum of 1 Al per 8 unit cells, each unit cell composed of nAl + (96 − n)Si (*21*). This underscores the potency of the Al(OH)Si site in the ZSM-5 framework. This study has also demonstrated that binding with alumina can generate active sites in the zeolite.

The isomorphous replacement of Si by B in the framework of ZSM-5 has been shown to give rise to weak Brønsted acidity (*14*, *22*). The acidity of the B(OH)Si site can be considered to be dependent on the position of the following equilibrium:



The present data, taken together with IR and TPAD studies (*14*), indicate that the equilibrium lies almost completely to the left. In comparison, the opposite is indicated for the Al(OH)Si site. Furthermore, the catalytic efficiency of the Al(OH)Si site in ZSM-5 in extremely dilute concentrations suggests that its affiliated proton is highly delocalized, and could plausibly be considered to approach a free proton in essence. Such a situation may be unique to dehydrated high-silica zeolites such as ZSM-5, whose interior environments are essentially homopolar.

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REFERENCES

1. Barrer, R. M., "Hydrothermal Chemistry of Zeolites," Chap. 6. Academic Press, New York, 1982.
2. Mobil Oil Corp., Belgium Patent 871,893 (1979).
3. Chang, C. D., Chu, C. T-W., Miale, J. N., Bridger, R. F., and Calvert, R. B., *J. Amer. Chem. Soc.* **106,** 8143 (1984).
4. Bragin, O. V., Vasina, T. V., Nefedov, B. K., Lutovinova, V. N., Alekseeva, T. V., and Minachev, Kh.M., *Izv. Akad. Nauk SSSR, Ser. Khim.* (5), 1179 (1981).
5. Bragin, O. V., Vasina, T. V., Nefedov, B. K., Lutovinova, V. N., Alekseeva, T. V., and Minachev, Kh. M., *Izv. Akad. Nauk SSSR, Ser. Khim.* (3), 626 (1982).
6. Bragin, O. V., Vasina, T. V., Nefedov, B. K., Preobrazhensky, A. V., Palishkina, N. V., Alekseeva, T. V., and Minachev, Kh.M., "Proceedings, 11th World Petroleum Congress, London, 1983," Vol. 4, p. 163 (1984).
7. Kutz, N., *in* "Proceedings, 2nd Annual IUCCP Research Symposium in Heterogeneous Catalysis" (B. L. Shapiro, Ed.). Texas A&M Univ. Press, College Station, Texas, 1984.
8. Ione, K. G., Vostrikova, L. A., Paukshtis, E. A., Yurchenko, E. N., and Stepanov, V. G., *Akad. Nauk SSSR* **27,** 1160 (1981).
9. Shihabi, D. S., Garwood, W. E., Chu, P., Miale, J. N., Lago, R. M., Chu, C. T-W., and Chang, C. D., *J. Catal.* **93,** 471 (1985).
10. Argauer, R. J., and Landolt, G. R., U. S. Patent 3,702,886.
11. Klotz, M., U.S. Patent 4,268,420.
12. von Ballmoos, R., and Olson, D. H., private communication.
13. Taramasso, M., Perego, G., and Notari, B., *in* "Proceedings, 5th International Conference on Zeolites, Naples, 1980" (L. V. Rees, Ed.), p. 40. Heyden, London, 1980.
14. Chu, C. T-W., and Chang, C. D., *J. Phys. Chem.*, in press.
15. Olson, D. H., Haag, W. O., and Lago, R. M., *J. Catal.* **61,** 390 (1980).
16. Bartley, B. H., Habgood, H. W., and George, Z. M., *J. Phys. Chem.* **72,** 1689 (1968).
17. Kiricsi, I., Hannus, I., Varca, K., and Fejes, P., *J. Catal.* **63,** 501 (1980).
18. Chang, C. D., and Silvestri, A. J., *J. Catal.* **47,** 249 (1977).
19. Chang, C. D., "Hydrocarbons from Methanol." Dekker, New York, 1983.
20. Chang, C. D., Chu, C. T-W., and Socha, R. F., *J. Catal.* **86,** 289 (1984).
21. Kokotailo, G. T., Lawton, S. L., Olson, D. H., and Meier, W. M., *Nature* (*London*) **272,** 437 (1978).
22. Scholle, K. F. M. G. J., Kentgens, A. P. M., Veeman, W. S., Frenken, P., and van der Velden, G. P. M., *J. Phys. Chem.* **88,** 5 (1984).
23. Ione, K. G., Vostrikova, L. A., Petrova, A. V., and Mastikhin, V. M., *in* "Structure and Reactivity of Modified Zeolites" (P. A. Jacobs, *et al.* Eds.), p. 151. Elsevier, Amsterdam, 1984.

24. Gabelica, Z., Nagy, J. B., Bodart, P., and Debras, G., *Chem. Lett.* 1059 (1984).

25. Hsu, J. T., Occelli, M. L., and Galya, L. G., AIChE 1984 Summer Natl. Mtg. (Phila. 8/19–22/84), Prepr. No. 42b.

26. West, P. B., Haller, G. L., and Burwell, R. L., Jr., *J. Catal.* **29,** 486 (1973).

27. Bourne, K. H., Cannings, F. R., and Pitkethly, R. C., *J. Phys. Chem.* **75,** 220 (1971).