

Tellurium-Loaded Zeolites

II. The Nature of the Dehydrocyclization Site

R. J. MIKOVSKY, A. J. SILVESTRI, E. DEMPSEY, AND D. H. OLSON

Mobil Research and Development Corporation, Research Department, Central Research Division, Princeton, New Jersey 08540

Received November 9, 1970

A study of the elution of tellurium from Te-NaX and Te-KX by hydrogen at elevated temperature has shown that the reducing atmosphere can prevent complete elution of tellurium from the catalyst. The inferred necessity of hydrogen for the formation of the aromatization site has been combined with the results of a separate crystallographic analysis and leads to a model for the active entity that rationalizes essentially all of our knowledge on these systems. The catalytically active entity is believed to be a tellurium ion, in the supercage of the zeolite base, coordinated to Site II and Site III cations. Support for this model comes from catalytic experiments designed to show the criticality of the presence of Site III cations.

I. INTRODUCTION

Tellurium in combination with certain zeolites yields highly selective, novel dehydrocyclization catalysts (1, 2). The best of these are obtained from the high-temperature treatment of physical mixtures of elemental tellurium and alkali-metal faujasites of low silica-alumina ratio.

The excellent selectivity for the aromatization of *n*-hexane that has been observed suggests that the active catalytic site is a well-defined entity with a definite geometric structure dependent upon the crystalline nature of the zeolite base. Furthermore, the previous work has led to the conclusion that the active tellurium is coordinated to the cations of the zeolite, a topic now to be further expanded.

We report here the results of experiments that fairly well reveal the character of the active entity. These experiments include a study of the long-term retention of tellurium (which tends to elute from the catalyst under reaction conditions), part of a single-crystal X-ray analysis, and a demonstration of the dependence of the aromatization activity upon the cation content of the zeolite.

II. EXPERIMENTAL

Catalysts were prepared by ball-milling (4 hr) physical mixtures of elemental tellurium and the zeolite. The mixtures were then pelleted and sized to 20-30-mesh particles.

The sodium-X zeolite was a Linde preparation (13X, L137518, 15.1% Na, 37.8% Al₂O₃, 47.4% SiO₂) that had a silica-alumina ratio of 2.45 and a Na-Al atom ratio of 0.99. The potassium-X base was prepared from the NaX by an ion-exchange procedure based on the sodium-potassium isotherm (3). Our standard sodium-X material was given five 2-hr exchanges at room temperature with 0.5 *N* potassium chloride solution. After having been washed free of chloride and calcined at 538°C, the material was found to have a potassium-to-sodium ratio of 23 (96% exchange).

The tellurium was finely divided material from Matheson, Coleman, and Bell that had assayed 99.5% tellurium.

The long-term retention studies were carried out in a cylindrical multitube furnace possessing ring heaters at each end. These ring heaters, together with a central heating element and proportioning tempera-

ture controller, established a constant temperature profile, $538^{\circ}\text{C} \pm 1^{\circ}$, across the central third of the furnace. Seven Vycor tubes, each containing 2.5 cm^3 of the appropriate pelleted and sized catalyst mix, extended through the furnace. Each catalyst sample could then be subjected to an individually metered and monitored flow of purified hydrogen or other eluting gas. The gas flow, throughout these experiments, was $30\text{ cm}^3/\text{min}$ under ambient conditions.

The procedure consisted of raising the furnace temperature to 538°C (~ 30 min) and maintaining conditions of temperature and hydrogen flow for 1 hr before establishing time zero. At this time a catalyst sample tube was removed from the furnace, cooled, and its contents were transferred to a glass vial under flowing hydrogen. Thereafter, samples were periodically removed from the furnace and treated similarly. Dehydrocyclization activity determinations were made on 1.5-cm^3 aliquots of the catalysts transferred from the glass vials into catalytic reactors in a helium-filled dry bag; thus the catalyst samples did not contact air between the elution experiments and activity determinations. The remaining 1.0 cm^3 of the samples was used for chemical analyses.

A standard activity test was established for comparison purposes. The test involved the aromatization of *n*-hexane and was carried out in a microreactor (2, 4). The pertinent conditions of the test were:

Temperature	510°C
Pressure	1 atm
Catalyst charge	1.5 cm^3 , 20-30 mesh
Carrier gas	Helium
Helium/hydrocarbon mole ratio	4/1
Contact time	9 sec (~ 0.5 LHSV)
Catalyst pretreatment	15 min at 510°C in flowing hydrogen
Length of test	2 hr, initial sample taken at 10 min on stream

The microreactor was equipped with a product sample loop so that total product analyses could be obtained chromatog-

raphically by diverting the chromatographic carrier gas through the sample loop.

Activities of the catalysts were taken to be the wt percent benzene detected in the gas phase by the chromatographic analyses. Analyses for "coke-on-catalyst" were combined with the gas-phase analyses to define an "absolute" selectivity, viz., the percentage of the converted *n*-hexane represented by a particular product, i.e., benzene, cracked material, or "coke."

Minor variations of this standard test were used to investigate the effect of cation content on aromatization activity. These variations and descriptions of the catalysts used are discussed in the appropriate section.

The chromatographic column was silicone oil (SF-96, 25%, 2.5 ft) on firebrick.

Tellurium contents of the catalysts were determined polarographically after digestion of the catalyst in strong acid.

III. RESULTS

A. Tellurium Retention and Catalytic Activity of Tellurium-Loaded NaX and KX

A series of four long-term retention experiments was carried out on tellurium-containing NaX and KX at 538°C and under flowing hydrogen. Two of these experiments were on a nominal 11 wt % Te-NaX and two were on samples of Te-KX of differing tellurium content.

The results, tellurium content versus stripping time, are given in Fig. 1. As shown, with the NaX-based catalyst, hydrogen treatment reduces the tellurium content, but after about 350 hr, a stationary tellurium level of about 3.5% is attained. The rate of tellurium loss in these two experiments, a relatively fast process in our studies, is still only about one-third of that to be expected if we were dealing with a simple transpiration process. On the other hand, with the KX-based catalysts, the elution rate was found to be much lower and was, in one case, essentially zero.

The initial aromatization activities, benzene yield (wt %) in standard aromatization test, for the Te-NaX and Te-KX system are compared in Fig. 2 as functions of tellurium contents. Included in the figure

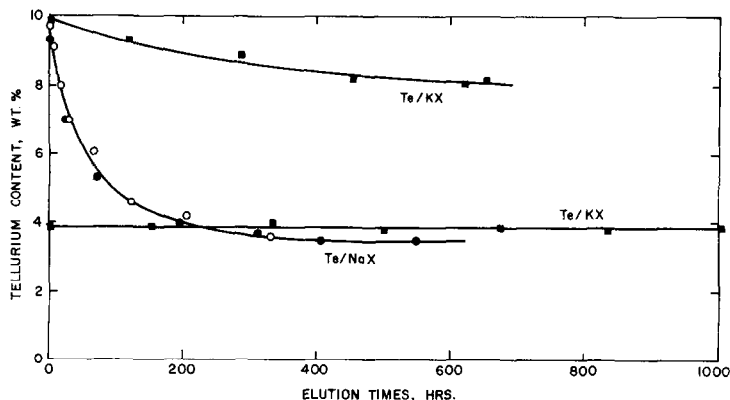


FIG. 1. Tellurium elution by hydrogen.

are data from both "freshly" prepared samples that had been exposed to flowing hydrogen for only 1 hr at 538°C and samples that had been subjected to long term hydrogen stripping. With Te-NaX, the activity appears as a function of the tellurium content independent of the length of hydrogen treatment. On the other hand, with Te-KX the activity increases with prolonged exposure to hydrogen at a given tellurium content. For example, with a 4% Te-KX, the benzene yield increases from 67 to 80% during about 600 hr of hydrogen treatment although the tellurium content remained constant. This may indicate that in the KX system the formation of optimum

coordination between the cations and tellurium is a relatively slow process.

The aromatization selectivity, benzene yield as a percentage of the converted *n*-hexane, for both the Te-NaX and Te-KX systems is shown in Fig. 3. Again, the data for Te-NaX represent both "fresh" catalysts and those subjected to long-term tellurium elution. The data for Te-KX represent only "fresh" catalysts although, with this system, the selectivity is independent of the long-term hydrogen treatment in contrast to the observed activities. The selectivity of Te-KX (92-97%) is found to be better than that of Te-NaX (90% optimum) and is much less dependent on tellurium content.

We present Figs. 2 and 3 for their qualitative features, allowing that a full discussion of the interrelation of activity, selectivity, deactivation and tellurium content is beyond

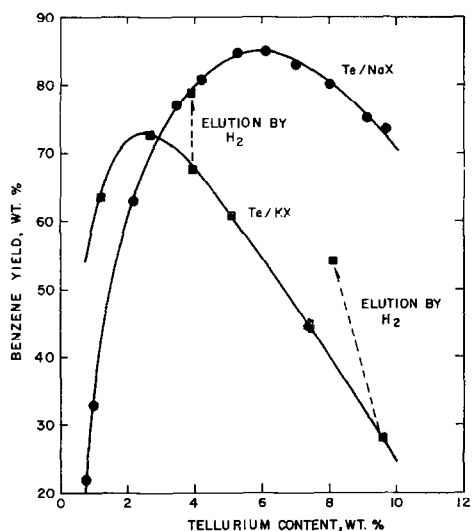


FIG. 2. Activity of Te-NaX and Te-KX.

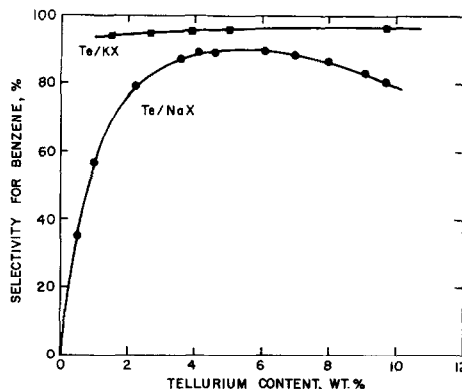


FIG. 3. Selectivity of Te-NaX and Te-KX.

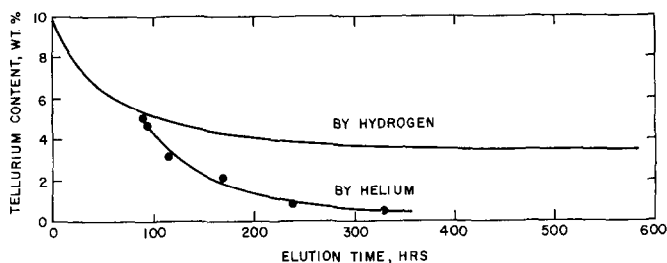


FIG. 4. Tellurium elution by hydrogen-helium.

our present intent. However, a capsule comparison of the behavior of the optimum Te-NaX and Te-KX catalysts in the aromatization test is as follows:

Catalyst	<i>n</i> -Hexane conversion (%)	Selectivity (%) for		
		Benzene	C ₁ -C ₅	Coke
6.0% Te-NaX	93	90	5	5
2.8% Te-KX	83	96	3	1

B. Influence of Elution Gas on Tellurium Retention

The work described in the previous section shows that with Te-NaX, in flowing hydrogen at 538°C, a stationary tellurium level of about 3.5% is attained. In order to establish the necessity for hydrogen in maintaining this stationary level a long-term retention experiment was carried out with the Te-NaX system in which the eluting gas was switched from hydrogen to deoxygenated* helium after the tellurium had been dispersed through the zeolite and eluted to just above the stationary level. The results of this experiment are given in Fig. 4 together with the previously determined curve for elution by hydrogen alone. Switching from a reducing to an inert elutant leads to an essentially complete loss of the tellurium from the zeolite in about 250 hr, indicating that hydrogen plays a necessary role in at least one mode of coordination between tellurium and the faujasite structure.

It is interesting to note that the elution by

* Previous information (1) and also our own work has shown that tellurium elution from Te-NaX by oxygen is nil, presumably due to formation of stable tellurium dioxide.

hydrogen of the tellurium in excess of the stationary level and the complete elution of all the tellurium in helium are both described by first-order decay processes, i.e., $(Te/Te_0) = e^{-\lambda t}$, with the same decay constant. These results, which are shown in Fig. 5, indicate that the interaction of the "excess" tellurium with the faujasite lattice is not as heavily dependent on hydrogen as is that of the stationary level tellurium.

We note that the activity and selectivity of the catalysts subjected to elution by hydrogen-helium are consistent with the results shown in Figs. 2 and 3.

C. X-Ray Crystallography

A crystallographic analysis has been performed on a single crystal of Te-NaX (5). Part of the results of this study form the

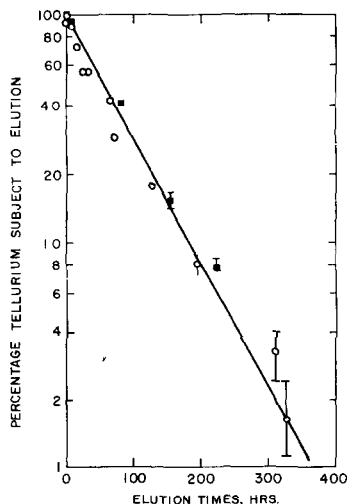


FIG. 5. Tellurium elution from Te-NaX: O, Tellurium in excess of that at steady state, under hydrogen; ■, Tellurium-on-catalyst, under helium.

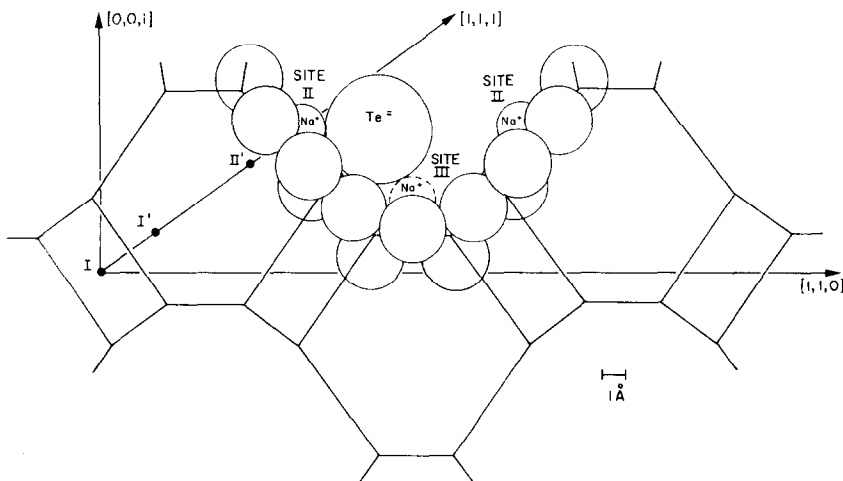


FIG. 6. Projection $(1, \bar{1}, 0)$ of Te-NaX structure. Solid lines, silicon-aluminum framework; circles, oxygen framework.

basis of our conclusions on the nature of the aromatization site.

The crystal was selected from a small batch of crystals that had been heated with tellurium (nominal 11% mix) to 538°C in helium. The chosen crystal was then treated in flowing hydrogen at 482°C in a capillary and subsequently sealed off, a procedure consistent with producing a good aromatization catalyst. The crystal was not analyzed for tellurium content; the calculated content, based on the crystallographic analysis, was 4.5 wt %.

In brief, tellurium was found both within the sodalite cage and within the supercage to the extent of five tellurium atoms per unit cell, approximately one tellurium atom in every six sodalite cages and one tellurium atom in every two supercages. Supercage tellurium is presumably the active aromatization entity due to its accessibility to reactant molecules. Furthermore, the tellurium was coordinated to the cations of the structure, the supercage tellurium to Site II cations and the tellurium in the sodalite cage to four Site I' cations.*

* Cation sites are understood to be as follows: (I) within the hexagonal prism; (II) in the supercage and on a hexagonal face of a sodalite unit; (I') and (II') within the sodalite unit, opposed to sites I and II, respectively; and (III) within the supercage, and conventionally centered on the square faces of sodalite units (6, 7).

The position of the supercage tellurium, as found in the analysis, is shown in Fig. 6, which is a projection of portions of both the silicon-aluminum framework and the oxygen framework on a $(1, \bar{1}, 0)$ plane, i.e., the plane of symmetry that runs through two neighboring six-rings, in a given supercage, and through the bridge of three four-rings connecting them. The tellurium was found next to a sodium ion nestled in the center of a six-ring (Site II), at a distance equal to the sum of the Pauling ionic radii for Na^+ and Te^{2-} . The unsymmetrical position of the tellurium suggested that an additional cation, at least, may be necessary for coordination to the tellurium. Failure to detect this additional cation by X-ray diffraction is the result of the low occupancy of the site.

The cation required for this added coordination may be supplied from those occupying Sites III, i.e., from those *supercage* cations that are in excess of the number of cations filling the more stable Site II. Unpublished X-ray studies (9) indicate that, in the dehydrated structure, the Site III cations are located near the edges of the square faces of the sodalite cage; conventionally, for reasons of symmetry, they are placed at the centers of the square faces (6, 7). Figure 6 shows that a sodium ion placed in the *conventional* Site III (dotted arc) lies at the appropriate distance from the observed position of the

tellurium and allows optimum coordination between the two species.

This structural evidence gives further indication that the tellurium is in the negative oxidation state (2).

D. Influence of Cation Content on Catalytic Activity

It has previously been shown that the silica-alumina ratio and the number of cations play a strong role in the dehydrocyclization activity of tellurium-loaded zeolites (1, 2). The model suggested above for coordination of tellurium by Site II and Site III cations implies the importance not only of the total number of cations, but more specifically that the presence and number of Site III cations in faujasites may be critical for catalytic activity, always assuming that the more stable Site II is filled. The number of such cations in alkali metal faujasites is that by which the total number of cations exceeds the population of all the other sites. The concentration of Site III cations may be effectively changed by varying the silicon-to-aluminum ratio, increasing the valency of the cation, or changing the total number of metal cations (e.g., by ion exchange with NH_4^+) so that on dehydration less cations assume the low stability Site III positions.

To illustrate the importance of the Site III cations, two series of experiments were performed with catalysts based on faujasites of various Site III cation concentrations. In the first series of experiments, the catalysts were all nominal 6 wt % tellurium catalysts prepared by the standard ball-milling technique, pretreated for 1 hr in flowing hydrogen at 538°C, and then subjected to the standard 510°C aromatization test. Table 1 lists the pertinent results along with the ion-exchange procedures used in modifying the zeolitic bases. We can readily see that those catalysts in which the number of Site III cations is low, either because of high silicon-to-aluminum ratio or because of replacement by protons, are poor catalysts in terms of both aromatization activity and tellurium retention.

If Site III cations were effective *only* in retaining tellurium, the above results could be explained by insisting that the catalysts that showed low activity did so because of their inability to hold tellurium; the question then arises, are the Site III cations necessary for activity regardless of tellurium content? We, therefore, carried out another series of experiments in which the catalysts concerned would have an "excess" tellurium content. In this series the catalysts, again, containing 6 wt % tellurium and based on faujasites of

TABLE 1
EFFECT OF SITE III CATIONS ON STANDARD ACTIVITY

Catalyst base	Si/Al	Approximate No. Site III cations per unit cell	Initial activity (wt % benzene)	Tellurium on spent catalyst (wt %)
NaX ^a	1.2	39	85.3	4.7
NaY ^b	1.9	18	55	4.4
NaHX ^c	1.2	4	<1	0.2
NaY ^d	2.8	2	~7	0.4
NaHY ^e	1.9	0	<1	1.5

^a Standard Linde 13X, L137518.

^b From J. M. Huber Corp.; Na = 10.9, Al₂O₃ = 26.1, SiO₂ = 58.3.

^c Standard 13X exchanged with NH₄Cl and dried at 100°C; Na = 9.8, Al₂O₃ = 34.9, SiO₂ = 54.2, N = 2.8, ash = 70.4. Ammonium decomposition effected by evacuating finished catalyst mix at 300°C for 30 min, then holding catalyst at 540°C in flowing hydrogen for 1.5 hr.

^d Synthetic NaY; Na = 9.4, Al₂O₃ = 20.3, SiO₂ = 66.7.

^e Exchange of Huber Y with NH₄Cl, air dried overnight; Na = 4.9, Al₂O₃ = 27.0, SiO₂ = 60.7, N = 1.41, ash = 72.3. Calcined in flowing helium for 5 hr at 450°C prior to milling with tellurium.

TABLE 2
EFFECT OF SITE III CATIONS ON DEHYDROCYCLIZATION ACTIVITY

Catalyst base	Si/Al	Approximate No. Site III cations per unit cell	Initial activity (wt % benzene)	Tellurium on spent catalyst (wt %)
NaX ^a	1.2	39	62	4.8
NaY ^b	1.9	18	32	4.9
NaHY ^c	1.9	0	4	4.3
NaY ^d	2.8	2	<1	4.9
CaX ^e	1.2	0	<2	4.9

^a Standard Linde 13X, L137518.

^b See footnote (b), Table 1.

^c Exchange of Huber Y as in footnote (e), Table 1, but to lesser degree; Na = 9.5, Al₂O₃ = 26.7, SiO₂ = 60.0, N = 0.7, ash = 73.2.

^d See footnote (d), Table 1.

^e Linde 13X, Lot 262, exchanged with CaCl₂; Ca = 13.4, Na = 0.2, Al₂O₃ = 33.1, SiO₂ = 49.8.

various Site III ion concentrations, were raised to 510°C as rapidly as possible under flowing hydrogen, held at that temperature for 5 min, and the activity tests were then performed with *hydrogen* carrier gas. Results of these experiments are listed in Table 2. Here it can be seen that while the tellurium contents of the spent catalysts are all relatively high (~5 wt %), the catalytic activity is still very low when the concentration of Site III cations is low.*

These results support the model proposed above and illustrate that with elemental tellurium and alkali-metal faujasites high catalytic activity can be obtained only when the number of Site III cations is relatively high.

IV. DISCUSSION

The criticality of Site III cations for dehydrocyclization activity immediately rationalizes an early generalization, viz., that the most favorable supports are those alkali-metal faujasites of low silica-alumina ratio. Support materials such as alkaline-earth faujasites, hydrogen-Y zeolite, rare-earth X, alumina, and silica, all (1, 2) show poor

dehydrocyclization activity, if any, and poor tellurium retention due to the inability to form the complex just described.

As mentioned above, the proposed coordination to which catalytic activity is ascribed implies that the tellurium is present in a negative oxidation state which further requires that cations be produced to maintain the electrical neutrality of the zeolitic structure. Hydrogen—either in the reactant mixture or produced by catalytic reactions—may furnish protons which can assume positions in the structure as proposed by Olson and Dempsey (8). The necessity of hydrogen in order to produce this state of the catalyst also sharply distinguishes it from the simple dispersion of tellurium throughout the zeolite that is produced by high temperatures in an inert atmosphere (e.g., helium).

A Te-NaX catalyst containing 0.4 wt % tellurium is about six times as active for cracking at 538°C as the NaX base and has very little aromatization activity (2). If this small amount of tellurium is accommodated by the zeolite *within* the sodalite unit, where it is inaccessible to reactant, the protons formed to maintain electrical neutrality may be responsible for the cracking activity, to the exclusion of aromatization activity. Further additions of tellurium, forming the aromatization site in the supercage, would then transform the activity from predomi-

* The first two catalysts of Tables 1 and 2 are essentially the same, respectively, in terms of support and tellurium content. The lower activities listed in Table 2 result from the use of hydrogen carrier gas, a routinely observed effect.

nantly cracking to dehydrocyclization, as is found (2).

The further development of this rationalization must consider the possible types, strengths, and geometric position of the acid sites involved. Tellurium coordination within both the supercage and the sodalite unit would necessitate the formation of protonic sites. The transformation of activity from cracking to dehydrocyclization with increasing tellurium content, even if a purely kinetic effect, would strongly reflect the character of the acid sites involved.

Differences between the Te-KX and Te-NaX systems may be rationalized by the constraint that a potassium-tellurium complex cannot form within the sodalite unit, a reasonable limitation in that the potassium ionic radius is greater than that of sodium. The absence of catalytically ineffective tellurium within the sodalite unit of the KX structure would lead us to expect an optimal activity, comparable to that of Te-NaX, at a lower tellurium level, as observed. Furthermore, with no contribution to aromatization or cracking derived from sodalite-cage tellurium, the selectivity would become

wholly dependent on the supercage tellurium, and would be essentially independent of tellurium content and length of hydrogen treatment. An obvious first step in testing the validity of this constraint would be a crystallographic study of the Te-KX system.

ACKNOWLEDGMENT

Our thanks are extended to G. F. Killmer for his able experimental assistance.

REFERENCES

1. MIALE, J. N., AND WEISZ, P. B., *J. Catal.* **20**, 288 (1971).
2. LANG, W. H., MIKOVSKY, R. J., AND SILVESTRI, A. J., *J. Catal.* **20**, 293 (1971).
3. SHERRY, H. S., *J. Phys. Chem.* **70**, 1158 (1966).
4. MIALE, J. N., AND WEISZ, P. B., *J. Catal.* **6**, 278 (1966).
5. OLSON, D. H., MIKOVSKY, R. J., SHIPMAN, G. F., AND DEMPSEY, E., to be published.
6. DEMPSEY, E., *Conf. Mol. Sieves, Soc. Chem. Ind., London, Chem. Eng. Group Proc.* 293 (1968); *J. Phys. Chem.* **73**, 3660 (1969).
7. BRECK, D. W., *J. Chem. Educ.* **41**, 678 (1964).
8. OLSON, D. H., AND DEMPSEY, E., *J. Catal.* **13**, 221 (1969).
9. OLSON, D. H., unpublished information.