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# Investigation of the Surface Structure and Activity of Molybdenum Oxide-Containing Catalysts

## I. An Infrared Study of the Surface Structure of Molybdena–Alumina Catalysts

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A comparison has been made of the infrared spectra of alumina with molybdenum oxide–alumina in both the oxidized and reduced forms. In the case of molybdena–alumina prepared via adsorption of gaseous $MoO_2(OH)_2$, the spectra show that a practically complete monolayer of $Mo^{6+}$ oxide covers the alumina. After reduction with hydrogen the hydroxyls of the carrier appear. From the reversibility of reduction and oxidation under mild conditions it has been established that the reduced oxide is present as an interrupted monolayer.

Catalysts prepared by adsorption of molybdate ions from solution contain Al hydroxyls, due to a lower Mo content.

## INTRODUCTION

Infrared studies of the surface of gamma alumina have been reported by various authors, at least five types of hydroxyl groups being detectable (*1*, *2*), and Peri (*3*) has proposed a model for the surface.

There have been correspondingly few ir studies on molybdena–alumina between 4000 and 1000 cm$^{-1}$. (*4*, *5*). However, other techniques have been employed, and some authors mention the formation of monomolecular molybdena–alumina catalysts. Russell and Stokes (*6*) observed that the dehydrogenation activity of molybdena–alumina catalyst increased linearly with Mo oxide content and then became constant. Assuming 15 Å$^2$ as the diameter of a $MoO_3$ unit, it was pointed out that the activity became constant when the alumina could just be covered totally be a monomolecular layer of the molybdenum oxide. Lipsch and Schuit (*7*) concluded that there was a spreading of $MoO_3$ on $Al_2O_3$ on the basis of results with reflectance spectroscopy. They proposed octahedral coordination for the molybdenum. Ashley and Mitchell (*8*), however, stated that the major part of the molybdenum is surrounded tetrahedrally, with only a small amount octahedral. Asmolov and Krylov (*9*) concluded that there was tetrahedrally surrounded molybdenum at low $MoO_3$ percentages, whereas octahedral molybdenum was detected at a higher content.

Some authors have discussed the existence of an aluminum molybdate (*9–12*). Also in our laboratory the formation of $Al_2O_3 \cdot 3MoO_3$ was found by means of X-ray diffraction when preparing the catalyst by passing gas phase $MoO_2\ (OH)_2$ through an alumina bed at 600°C. Provided adsorption times are not too long the main part of the alumina bed contains a constant percentage of molybdenum oxide. Calculation of the mean surface area per molybdenum oxide molecule and comparison with the diameter of $MoO_3$ when monomolecular adsorption is assumed to take place predominantly on (100) face exposures of the gamma alumina gives reason to conclude a total coverage of the alumina by $MoO_3$ (*13*).

This paper describes the structure of molybdena–alumina prepared by two methods. The results support our view that the $MoO_3$ is spread out during preparation and prove that it remains on top of the alumina under reducing circumstances. Detailed information is given about the structure of the reduced catalyst.

## EXPERIMENTAL METHODS

### *a. Preparation of the Catalyst*

*Preparation by gas phase adsorption of molybdenum oxide.* The mixed oxide catalyst was prepared in the following way: a flow of air of about 15 liters $hr^{-1}$ was saturated with water vapor up to 375 Torr. The mixture was passed first through a bed of $MoO_3$ particles of about 15 cm high at a temperature of 595°C. Under these circumstances gaseous $MoO_2(OH)_2$ is formed with a partial pressure of 0.15 Torr. Then the mixture was led through a bed of Degussa alumina particles ($78\ m^2\ g^{-1}$) of about 10 g at 600°C. It took 2 days before the molybdenum oxide broke through. The main part of the bed contained about 10.2% $MoO_3$ by weight. For further details see Ref. (*13*).

*Preparation in the liquid phase.* A fresh solution of ammonium molybdate in $HNO_3$ ($pH = 1$) was passed through a bed of Degussa alumina particles. The molybdenum oxide content after drying at 500°C during 1 hr was found to be 9.3% by weight. For further details see Ref. (*13*).

### *b. Infrared Experiments*

Self-supporting tablets were made by pressing 100 mg of material at about 1.5 tons/$cm^2$. The discs, which had a diameter of 2.5 cm, were placed in a cell in which further preparations could be carried out *in situ.* After removal of oxidizable impurities by a stream of pure oxygen at 450°C, the discs were calcined by evacuation at 450°C or reduced in a stream of purified hydrogen for several hours, and then evacuated, mostly at pressures lower than $10^{-5}$ Torr, in order to remove water.

Infrared measurements were carried out on a Grubb Parsons "Spectromaster" (MK III). In most measurements the spectrum had to be expanded in the transmission direction and also an attenuation comb had to be placed in the reference beam because of the low transmission of the disc. All infrared experiments were carried out at room temperature.

Because of the low transmission in the OH region and to avoid spectral disturbance by atmospheric water, the OH hydrogen was mostly exchanged with deuterium either by keeping the disc in an atmosphere of oxygen saturated with $D_2O$ ($p = 15$ Torr), when measurements had to be done with the oxidized catalyst, or in deuterium gas with a pressure of about 250 Torr. Temperature was 450°C. Care was taken in order that all OH groups had been transformed into OD groups by checking the OH region of the infrared spectrum.

### *c. Reduction Measurements*

The valence of the molybdenum ions was determined by means of oxidation by sodium periodate to Mo(VI). By titration of the formed iodate the average degree of oxidation of molybdenum in the sample can be established (*14*).

### *d. Determination of the Amount of OH Groups*

The procedure for determining the amount of OH groups by means of reaction with methylmagnesium iodide was that described by Fripiat and Uytterhoeven (*15*).

## RESULTS

### *a. The Deuteroxyl Groups on Alumina*

Degussa alumina was treated with steam at 600°C, similar to the preparation of the molybdenum oxide catalyst by vapor adsorption of $MoO_2(OH)_2$.

The spectrum of the OD groups is shown in Fig. 1; after evacuation at 450°C during several hours three bands can be observed, the positions of which are in accordance with previous work (*16*). All three bands are due to stretching vibrations, as may be concluded from the ratio of their frequency to those of the corresponding hydroxyls. This turns out to be 0.738, which means that these vibrations can be described with the harmonic oscillator model.

Treatment of the original hydroxyl groups either with $D_2$ or with $D_2O$ yields, as may be expected, the same deuteroxyl groups.

### *b. The Behavior of the Deuteroxyl Groups on a Gas Phase Prepared Molybdena–Alumina Catalyst with a Molybdenum Valence near 6*

Figure 2 shows the OD spectrum after having kept the disc in $D_2O$ and oxygen at 350–450°C. The oxygen is necessary to avoid reduction of the molybdenum ions which mostly occurs upon heating in an inert atmosphere at higher temperatures.

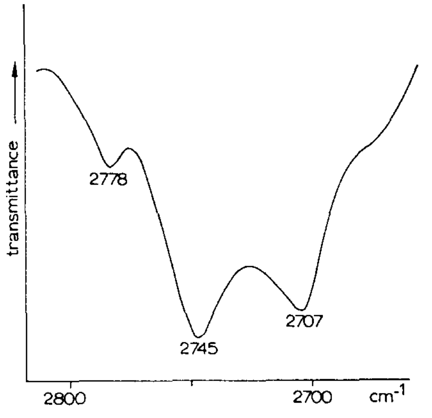

FIG. 1. Infrared spectrum of steam-treated alumina after reaction with $D_2O$ or $D_2$ at 450°C and subsequent evacuation during 12 hr at the same temperature ($p = 10^{-5}$ Torr).

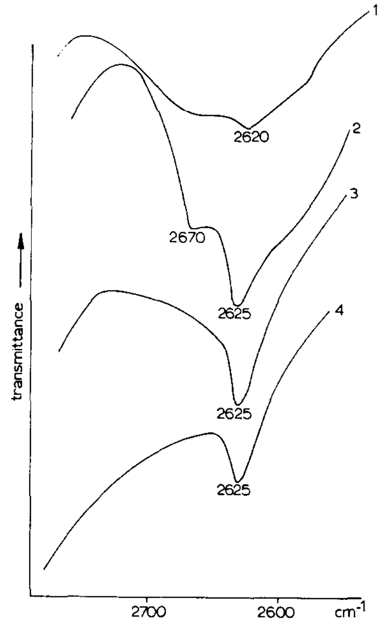

FIG. 2. Evacuated molybdena-alumina prepared by the gas phase method. The Mo valence was between 5 and 6. (1) Reaction at 350, 400 and 450°C with $D_2O$ in an oxygen atmosphere and evacuation during 30 min at the corresponding temperatures yields approximately the same results. (2) and (3) After prolonged evacuation ($p = 10^{-5}$ Torr) during another 15 or 30 min at 450°C. (4) After prolongation of the same treatment for 90 min. (For clarity, in Figs. 2 and 3 the spectra have been translated in the transmission direction.)

After this treatment and evacuation at the temperatures indicated, only one band around 2620 cm$^{-1}$ could be detected together with a shoulder at 2670 cm$^{-1}$. Even after prolonged evacuation at 450°C and $10^{-5}$ Torr, no other spectral change occurs than that the 2670 cm$^{-1}$ shoulder tends to disappear (Fig. 2) and that the band around 2620 cm$^{-1}$ shifts to a somewhat higher frequency. We have no explanation for the disappearance of the 2670 cm$^{-1}$ band. It is clear that the 2625 cm$^{-1}$ band has a considerable band width.

After these experiments the molybdenum valence was between 5 and 6. The color had changed from yellowish to brownish-black.

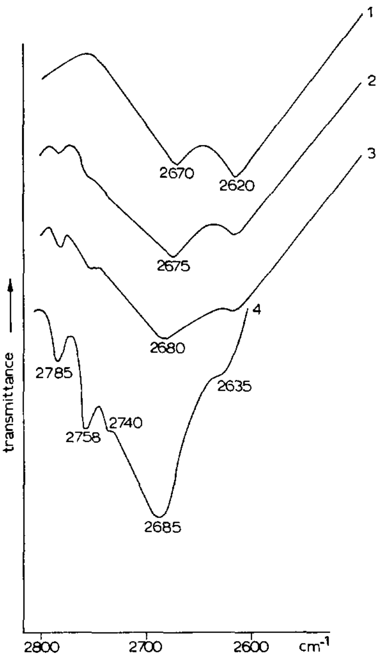

FIG. 3. The behavior of the deuteroxyl groups of gas phase prepared molybdena–alumina under reducing circumstances. (1) After reduction with deuterium gas ($p$ = 250 Torr) at 350°C for 15 min, followed by evacuation at the same temperature during 2.5 hr. (2) Same procedure at 400°C. (3) As for (1), but the reduction time amounted to 10 min at 450°C. (4) As (3), but after reduction with $D_2$ during another 10 min at 450°C.

### *c. The Deuteroxyl Groups on Gas Phase Prepared Molybdena–Alumina during Reduction to a Molybdenum Valence Near 4*

The spectra in Fig. 3 show the behavior of the OD groups after reduction with deuterium at a pressure of 25 cm Hg. The 2670 cm$^{-1}$ band increases remarkably and shifts to higher frequencies when the treatment is carried out at higher temperatures. Simultaneously the band at 2620 cm$^{-1}$ disappears. In the higher frequency region bands are observed which resemble those of pure alumina. However, there is an extra band found near 2755 cm$^{-1}$.

### *d. The Deuteroxyl Groups on a Catalyst with a Molybdenum Valence of 4*

Figure 4 shows the deuteroxyl bands after reduction during 24 hr in a stream of pure hydrogen at 450°C. The molybdenum valence proved to be four.

The most important fact to be noted is that at least three of the four observed bands have approximately the same positions as those for pure alumina. Only the band at 2755 cm$^{-1}$ can be attributed to the influence of molybdenum oxide.

### *e. Some Experiments Pertaining to the Reproducibility of the Spectra*

One could suggest that reduction involves a remarkable change in the microscopic surface composition, e.g., the formation of crystalline $MoO_2$. In that case reoxidation of the surface under mild conditions would not provide the same OD absorption spectra as that before reduction and reoxidation. The experiments show, however, that treatment with $D_2O$ and oxygen at moderate temperatures (<400°C)

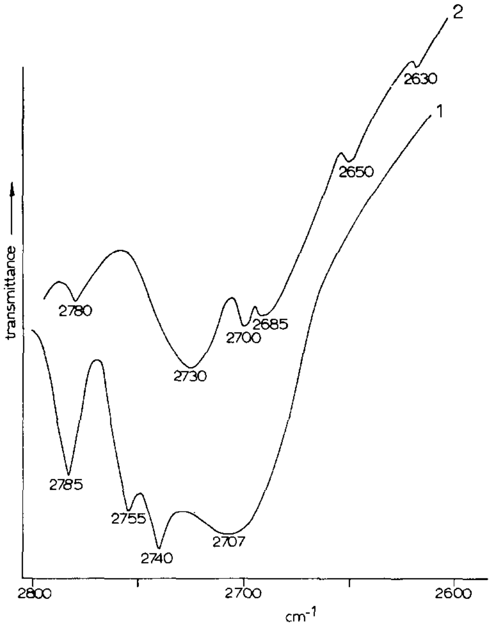

Fig. 4. (1) Gas phase prepared molybdena-alumina, reduced in a stream of hydrogen at 450°C during 24 hr, followed by exchange with $D_2$ and evacuation during 10 hr at the same temperature ($p$ = $10^{-5}$ Torr). (2) Mo(VI) oxide alumina prepared by adsorption from solution at pH 1, after evacuation at 450°C.

and evacuation, yields about the same band position as found in the freshly prepared catalyst.

It turns out that treatment with $D_2O$ at 450°C does not significantly affect the OD group spectra, either for the $Mo^{4+}$ form (Fig. 4) or the partially reduced ones (Fig. 3). This is in contrast with the findings of Massoth (*17*) that $H_2O$ is able to oxidize $Mo^{4+}$.

### *f. The Catalyst Prepared from the Liquid Phase*

Some investigations have been made with an $Mo^{6+}$ catalyst prepared at pH 1, which contained 9.3% by weight of $MoO_3$.

The spectrum of this species contains both the OD absorption bands found on alumina and those of the gas phase prepared oxidized molybdena–alumina catalyst (see Fig. 4, Curve 2).

## DISCUSSION

### *a. The OD Groups on Alumina*

As has been stated, the three bands in Fig. 1 belong to approximately freely vibrating OD groups. There is a difference between the shapes and relative sizes of the bands when comparing them with those of the alumina not pretreated with steam: in the latter case the 2707 $cm^{-1}$ band is the most intense one, while steam treatment causes comparable sizes for the bands at 2707 and 2745 $cm^{-1}$. The latter behavior is in accordance with that reported by Peri (*2*). We also found that the relative sizes of these two bands are dependent on time and temperature of evacuation. In contradiction to Peri's findings, however, our highest frequency band is more like a shoulder than a free band. The reason is that he used much higher evacuating temperatures, which also explains the higher frequencies of all three bands found by him previously and the fact that in later experiments he could detect even five bands (*1, 2*).

### *b. The Deuteroxyl Groups on a Gas Phase Prepared Molybdena–Alumina with a Molybdenum Valence near 6*

We wondered if evacuation could cause a considerable reduction of the molybdenum oxide or not, for evacuation at about 400°C changes the color of the catalyst from yellowish to brownish-black. As stated earlier, determination of the valence of Mo after reduction of the Mo(VI) oxide–$Al_2O_3$ catalyst merely by evacuation at moderate temperatures yielded values between 5 and 6. Repeated evacuation and reoxidation, however, slows down the rate of change in color caused by this reduction. Both the constancy of the $MoO_3$ percentage in the bed and its calculated diameter value after gas phase preparation of the catalyst point to a complete monomolecular layer of molybdenum oxide on alumina (*13*). Moreover, the fact that the spectrum of this molybdena–alumina evacuated at higher temperatures does not contain bands present in that of alumina (Fig. 2) proves also that the coverage of the alumina by molybdenum oxide is reasonably complete.

The observed 2625 $cm^{-1}$ band corresponds with a 3550 $cm^{-1}$ band when dealing with a hydroxyl group which is absent on alumina. In the literature (*18*) it is stated that analogous low positions of OH bands in zeolites must be attributed to interactions with the lattice due to special positions. In our case, the 3550 $cm^{-1}$ band is indeed present on nondeuterated molybdena–alumina. We now suggest that the 2625 $cm^{-1}$ vibration originates from a structural OD group on an aluminum species and interacting with the molybdenum oxide layer on top of the alumina.

The absence of undisturbed $Al_2O_3$ hydroxyls in the spectra of the OH groups after evacuation therefore supports the conclusion that the coverage of the aluminum oxide by the molybdenum oxide is reasonably complete and that (even) a slight reduction of the molybdenum does not significantly damage this completeness.

### *c. The Deuteroxyl Groups on Reduced Gas Phase Prepared Molybdena–Alumina*

The spectra in Fig. 3 show the change of the deuteroxyl group frequencies on reducing with deuterium at increasing temperatures. Prolonged reduction at 450°C yields a valence of about 4 for the molybdenum ions. The spectrum of this reduced catalyst (Fig. 4) had to be expanded enormously, the concentration of OH groups being very low: chemical analysis showed the presence of 1 OH group/100 $Å^2$ after prolonged evacuation, while on the surface of alumina under the same circumstances about 5 OH groups/100 $Å^2$ are found. Moreover, the background absorption has increased very considerably.

Analysis of the spectrum of the fully reduced catalyst shows that at least three of the four bands found in the OD group frequency part may be attributed to OD groups on alumina: their positions correspond very well and, moreover, the behavior of the bands at 2707 and 2740 $cm^{-1}$ with respect to evacuation and temperature treatment resembles the corresponding bands found on bare alumina.

The only discrepancy is that the relative size of the 2778 $cm^{-1}$ band found on alumina is smaller than that of the 2785 $cm^{-1}$ band on reduced molybdena–alumina. This may be caused by the possible adsorption preference of (reduced) molybdenum oxide for special places on the alumina. Peri suggested (*3*) that the highest frequency OH groups are the most basic ones. In our opinion the assumption that the acidic molybdenum oxide should react preferably with the most basic OH groups on $Al_2O_3$ is very reasonable. This could suggest that the highest frequency band corresponds with the most acid OH groups, in agreement with Dunken and Fink (*19*). The somewhat higher frequency of this band even indicates that the presence of $MoO_2$ diminishes the distortion of the corresponding hydroxyls compared with the results obtained from pure alumina.

As for the band around 2755 $cm^{-1}$ one could suppose it to be a distortion of the 2785 $cm^{-1}$ band. However, also an attribution to an OD group on $Mo^{4+}$ might be correct.

### *d. The Catalyst Prepared from Solution*

Some experiments (not reported here) have been made pertaining to the catalytic activities of the gas phase and of the solution prepared catalysts. The aim was to detect whether or not the nature of the chemisorbed molybdenum ions differ. It was found that the catalytic activities for pentene hydrogenation and isopropanol dehydration per Mo atom do not differ for the two kinds of catalyst but are far less than those of the surface ions of pure Mo oxide. This indicates that the differences in the spectra (Figs. 2 and 4, Curve 2) are merely due to incomplete Mo coverage in the case of solution-prepared catalysts.

### *e. The Transformation of the Monomolecular Layer under Reducing Circumstances*

As already shown, the reduced gas phase prepared catalyst exhibits Al hydroxyls, whereas the oxidized form does not. Moreover, repeated reduction and oxidation of the catalyst resulted in two changes in behavior: the reduction rate tends to diminish and so does the transmission of the fully reduced form. One might therefore suggest that ir spectroscopy has enabled some irreversible change during oxidation/reduction to be detected. Possibilities are:

i. $Mo^{4+}$ may migrate into the alumina lattice, causing a return of the Al-OH groups;

ii. crystallization of reduced molybdenum oxide may occur.

However, there are three arguments to reject these possibilities. They are as follows:

(a) a bulk migration or a recrystallization of $Mo^{4+}$-ions would cause an irreversible decrease of catalytic activity after prolonged reduction and heating at 450°C, but this has not been found; (b) migration and/or recrystallization could be reflected by an appearance of detectable X-ray spectral lines of a new chemical compound, or of $MoO_2$, a phenomenon which has not been observed even after long reaction times; (c) our experiments show a good reproducibility of the OD spectra after oxidation and reduction under mild conditions. When migration of $Mo^{4+}$ into the alumina lattice or formation of $MoO_2$ crystals occur, reoxidation at moderate temperatures cannot be expected to yield the same OD spectra as those of the freshly prepared (partially reduced) catalyst. The conclusion must therefore be that the monomolecular layer shrinks by reduction.

Some investigators conclude from their experiments that $Mo^{6+}$ is mostly tetrahedrally surrounded by oxygen ions (*8*, *9*), whereas $Mo^{4+}$ has been proven to be always octahedrally incorporated (*20*). An example of this is visualized in Fig. 5 where, neglecting the nature of the exposed crystallographic layers, the result of reduction and stabilization into an octahedral $Mo^{4+}$ oxide is given. The shrinkage may be caused by the fact that the Mo ions share oxygens after reduction due to a coordination change: angular and edge sharing may then occur.

The fact that the OH groups on the exposed alumina of the gas phase prepared catalyst are not disturbed by the lattice (Fig. 4, Curve 1) points to the presence of relatively large breaks in the $Mo^{4+}$ oxide layer, caused by the migration of $Mo^{4+}$ ions to octahedral sites. There are many studies concerning the O–H...O interaction in solids in correlation with the infrared frequency shifts caused by hydrogen bonding (*21*). Assuming an O–H...O interaction as the most probable one in our case we must conclude that on the reduced catalyst, not showing such an interaction, the monolayer breaks should always have a width of not less than 6 Å. In the case that the $Mo^{4+}$ ions form a discontinuous surface layer, one may even speak of an island structure on the carrier. An indication about the fraction of the total surface area which consists of alumina can be derived from the amount of OH groups detected (see above). If these OH groups are only present on the alumina, then we must conclude that 20% of the carrier becomes bare by reduction.

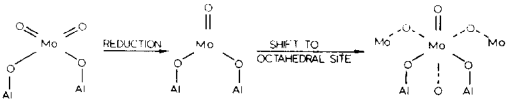

FIG. 5. Reduction of tetrahedral $Mo^{6+}$ oxide to octahedral $Mo^{4+}$ oxide on top of an alumina surface.

## CONCLUSIONS

1. A Mo(VI) oxide–$Al_2O_3$ catalyst, prepared by adsorption of gaseous $MoO_2(OH)_2$ at 600°C, is characterized by a more or less complete monomolecular layer of Mo(VI) oxide on top of the alumina.
2. The shrinkage of the surface area of molybdenum oxide by reduction with hydrogen causes the monolayer to break, so that part of the $Al_2O_3$ surface becomes bare.
3. The behavior of the spectra of molybdena–alumina prepared from solution is understood very well because of its lower molybdenum oxide percentage; the coverage is not complete, and therefore already on the oxidized catalyst hydroxyls of alumina are present.
4. The OH group spectrum shows a quite heterogeneous character for the surface, especially in the case of the reduced form.

## REFERENCES

*1.* Peri, J. B., and Hannan, R. B., *J. Phys. Chem.* **64**, 1526 (1960).

*2.* Peri, J. B., *J. Phys. Chem.* **69**, 1, 211 (1965).

*3.* Peri, J. B., *J. Phys. Chem.* **69**, 1, 220 (1965).

*4.* Farne, G., and Pernicone, N., *Accad. Naz. Lincei, Ser. 8*, XLIV, fasc. **4**, 560 (1968).

*5.* Kiviat, F. E., and Petrakis, L., *J. Phys. Chem.* **77**, 10, 1232 (1973).

6. Russell, A. S., and Stokes, J. J., Jr., *Ind. Eng. Chem.* **38**, 1071 (1946).
7. Lipsch, J. M. J. G., and Schuit, G. C. A., *J. Catal.* **15**, 174 (1969).
8. Ashley, J. H., and Mitchell, P. C. H., *J. Chem. Soc. A* 2730 (1969).
9. Asmolov, G. N., and Krylov, O. V., *Kinet. Katal.* **11**, 1028 (1970), Engl. transl. p. 847.
10. Doyle, W. P., and Forbes, F., *J. Inorg. Nucl. Chem.* **27**, 1271 (1965).
11. Ishii, Y., and Matsuura, I., *Technol. Rep. Kansai Univ.* **61**, 41 (1966).
12. Stork, W. H. J., Coolegem, J. G. F., and Pott, G. T., *J. Catal.* **32**, 3, 497 (1974).
13. Sonnemans, J., and Mars, P., *J. Catal.* **31**, 209 (1973).
14. Bourret, P., Lecuire, J. M., and Weis, C., *Chim. Anal.* (*Paris*) **52**, 48 (1970).
15. Fripiat, J. J., and Uytterhoeven, J., *J. Phys. Chem.* **66**, 800 (1962).
16. Scholten, J. J. F., Mars, P., Menon, P. G., and Van Hardeveld, R., *Proc. Int. Congr. Catal., 3rd, 1964* **2**, 281 (1965).
17. Massoth, F. E., *J. Catal.* **30**, 204 (1973).
18. Breck, D. W., "Zeolite Molecular Sieves." p. 460. Wiley, New York, (1974).
19. Dunken, H., and Fink, P., *Z. Chem.* **6**, 5, 194 (1966).
20. Kihlborg, L., *Ark. Kemi* **21**, 44, 471 (1963).
21. Pimentel, G. C., and McLellan, A. L., "The Hydrogen Bond," pp. 88–89. Freeman, San Francisco, Calif. (1960).