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# Studies on Molybdena Catalysts

## XI. Oxygen Chemisorption on Sulfided Catalysts

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Catalysts containing Mo or CoMo on various supports were prepared. Oxygen chemisorption on the sulfided catalysts was measured by a flow gravimetric technique. Activities of the catalysts were determined for thiophene hydrodesulfurization (HDS) and hexene hydrogenation in a catalytic microreactor at atmospheric pressure. Oxygen chemisorption increased with adsorption temperature. A definite adsorption was only obtained at −78°C, adsorption at higher temperatures continuing for over 4 hr. For $O_2$ chemisorption at −78°C: (i) CoMo versus Mo catalysts showed only marginally higher values; (ii) $O_2$ chemisorption did not correlate with HDS activity; and (iii) $O_2$ chemisorption showed a reasonable correlation with hydrogenation activity. It is probable that $O_2$ chemisorption reflects the general state of dispersion of the active Mo phase rather than specific HDS or hydrogenation sites.

## INTRODUCTION

Chung and Massoth (*1*) were among the first to report $O_2$ chemisorption values for sulfided CoMo/$Al_2O_3$ catalysts. Using a flow microbalance technique at 0°C, they showed that the $O_2$ uptake was: (i) proportional to Mo content in Mo/$Al_2O_3$ catalysts; (ii) small and essentially independent of Co content in Co/$Al_2O_3$ catalysts; and (iii) essentially independent of Co level in CoMo/$Al_2O_3$ catalysts of constant Mo content, and only slightly greater than the comparable Mo/$Al_2O_3$ catalysts of constant Mo content. The latter result was independent of the mode of catalyst preparation. Subsequent thiophene hydrodesulfurization (HDS) measurements on these catalysts (*2*) showed appreciable variations in HDS activities of the CoMo/$Al_2O_3$ catalysts and much lower activity for the Mo/$Al_2O_3$ catalyst. These results showed that $O_2$ chemisorption was not directly related to HDS activity, and it was tentatively concluded that if $O_2$ chemisorption was occurring on active HDS sites, then the presence of Co does not affect the number of active sites but rather their intrinsic activity.

Tauster *et al.* (*3*) have employed an $O_2$ pulse technique at ambient temperature to measure $O_2$ chemisorption on a number of unsupported $MoS_2$ samples. They found a direct correlation between $O_2$ adsorption and HDS activity for dibenzothiophene. On the basis that edge sites of $MoS_2$ crystals should selectively adsorb $O_2$ in preference to basal sites, they concluded that the edge sites are the active HDS centers, contrary to earlier findings of Stevens and Edmonds (*4*). (See also Refs. (*5*) and (*6*) on continuing discussion of this point.) In further limited studies, Tauster and Riley have suggested that the pulse $O_2$ chemisorption technique is also promising for characterization of supported CoMo catalysts (*7*) and coked catalysts (*8*).

In an attempt to resolve these differences, we undertook further studies of $O_2$ chemisorption, in particular, investigating the effect of adsorption temperature, comparison of $O_2$ chemisorption with catalytic activity for different catalysts, and effects of pyridine and coke.

## EXPERIMENTAL

Catalysts containing 8% Mo or 3% Co 8%

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Mo on various supports were prepared by incipient wetness impregnation followed by calcination at 540°C. For the CoMo catalysts, Mo was added first (ammonium paramolybdate), and the catalyst was heated to 110°C before adding the Co (cobalt nitrate). The following commercial catalysts were also tested: 2.75% Co 9.7% Mo/$Al_2O_3$; Topsøe—8% Mo/$Al_2O_3$ and 3% Co 8% Mo/Al (same $Al_2O_3$ support); and Ketjenfine 124, 1.5E—3% Co 8% Mo/$Al_2O_3$.

A flow gravimetric technique (*2*) was used to measure $O_2$ adsorption, except that adsorption temperatures of −78, 0, and 24°C were used by application of a suitable bath surrounding the reactor. Measured internal temperatures with a thermocouple were close to the respective bath temperatures. Although helium was purified by passing through a Hydrox purifier followed by a molecular sieve trap, a small and continuous weight gain was observed when passing over the sulfied catalyst at −78°C. This was eliminated by employing an activated charcoal-molecular sieve trap held at liquid $N_2$ temperature in the He line just prior to the reactor inlet.

Catalyst charges of about 150 mg of 20–40 mesh size, contained in a fine mesh gold cylinder, were used in the microbalance. Catalysts were sulfided in 9% $H_2S/H_2$ at 400°C for 2 to 4 hr, followed by a 1- to 2-hr flush in He. After lowering to the desired adsorption temperature in He, a 5% air/He mixture was admitted at a flow of about 125 $cm^3$/min, and the weight gain recorded. Preliminary results showed no difference in $O_2$ chemisorption values with air/He mixtures between 5 and 20% air. Some physical adsorption of $O_2$ on the catalysts at −78°C was evidenced by a weight loss (~0.9 mg/g for the CoMo Topsøe catalyst) after switching back to He. The net chemisorption was usually taken as the difference in weight in He before and after $O_2$ exposure. In some cases, the weight data were corrected for physical adsorption to generate chemisorption curves. All chemisorption values reported were obtained at −78°C.

For the effect of pyridine on $O_2$ chemisorption, the presulfided catalyst was subjected at 350°C to an He stream saturated with pyridine at 0°C. Following a 1-hr He flush to remove weakly bound pyridine, the temperature was lowered to −78°C and $O_2$ adsorbed as before. Different amounts of added pyridine were accomplished by varying the time of exposure.

Adsorption of $O_2$ was also measured on sulfided catalysts after exposure to a thiophene/$H_2$ mixture at 350°C for an overnight period. The latter hydrodesulfurization reaction is accompanied by a small amount of coke on the catalyst. These tests were done in the flow microbalance reactor under identical conditions as employed in the catalytic activity tests.

Catalysts were tested for HDS and hydrogenation activity in a fixed bed microreactor at atmospheric pressure as previously described (*9*). Catalysts were presulfided in 9% $H_2S/H_2$ at 400°C for 2 hr, followed by a 1-hr flush in He. Conversion of thiophene to butenes and butane, and hexene-1 to hexane was used to assess HDS and hydrogenation activities, respectively. A catalyst charge of 0.5–1.0 g of 20–40 mesh size mixed with 3 g of glass beads was employed. Catalysts containing CoMo were tested at 350°C, and Mo catalysts at 400°C. Conversions were measured after exposing the catalyst to a thiophene/$H_2$ flow overnight to achieve catalyst line out. Appropriate rate constants were calculated from the conversion data as described previously (*9*).

## RESULTS

The effect of adsorption temperature on the rate of $O_2$ adsorption for Topsøe Mo and CoMo catalysts is shown in Fig. 1. The first point to note is that with either catalyst, a definite weight line out was obtained at −78°C, but not at the higher temperatures, even after 4 hr. Second, virtually the same uptake was obtained for the two catalysts at −78°C, although at the higher temperatures, the CoMo/$Al_2O$ catalyst gave

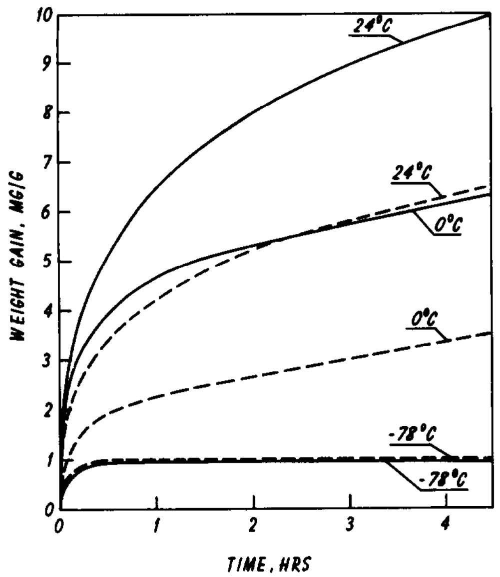

FIG. 1. Oxygen chemisorption on Topsøe CoMo/$Al_2O_3$ (——) and Mo/$Al_2O_3$ (- -) catalysts. Weights corrected for physical adsorption of $O_2$.

greater weight pickup. The chemisorption values at −78°C were 0.97 mg/g for the Mo catalyst and 0.94 mg/g for the CoMo catalyst. Chemisorption measurements on samples of the same catalysts using a volumetric technique at −78°C gave values of 1.44 and 1.11 mg/g, respectively (*10*). Although the values for the two techniques were somewhat different, the presence of Co did not significantly affect $O_2$ chemisorption.

Pyridine poisoning tests were performed on the Cyanamid CoMo/$Al_2O_3$ catalyst. Figure 2 shows that preadsorbed pyridine reduced the $O_2$ adsorption capacity of the catalyst in an almost linear manner.

Table 1 presents results of $O_2$ adsorption for various catalysts exposed to thiophene/$H_2$ at 350°C overnight. Values of coke added are also given. It is clear that significant additional $O_2$ chemisorption on the coked catalysts occurred, although these did not directly relate to the amount of coke added. As shown in Fig. 3, further slow continued uptake of $O_2$ was observed for these catalysts after an initial rapid pickup, in contrast to the sulfided catalysts (−78°C curves in Fig. 1). The values reported in Table 1 were estimated by extrapolation of the slow adsorption line back to meet the fast adsorption line.

TABLE 1

Effect of Coke on Oxygen Chemisorption for Different Catalysts

| Catalyst | Oxygen chemisorption [mg/g] | | Amount of coke [mg/g] |
|---|---|---|---|
| | Sulfided catalyst | Coked catalyst | |
| γ-$Al_2O_3$ | 0.00 | 0.22 | 12.1 |
| Co/γ-$Al_2O_3$ | 0.00 | 0.13 | 0.1 |
| Mo/γ-$Al_2O_3$ (Topsøe) | 0.97 | 2.55 | 2.5 |
| CoMo/γ-$Al_2$ (Topsøe) | 0.94 | 1.29 | 2.3 |

Catalysts containing Mo and CoMo on different supports and the commercial catalysts were tested for thiophene HDS and hexene hydrogenation activities. Table 2 lists the catalysts employed and the resultant $O_2$ chemisorption values on the sulfided catalysts. Except for the Topsøe catalyst, $O_2$ chemisorption values for the laboratory-prepared catalysts were somewhat higher when Co was present. Figures 4 and 5 present correlations of HDS and

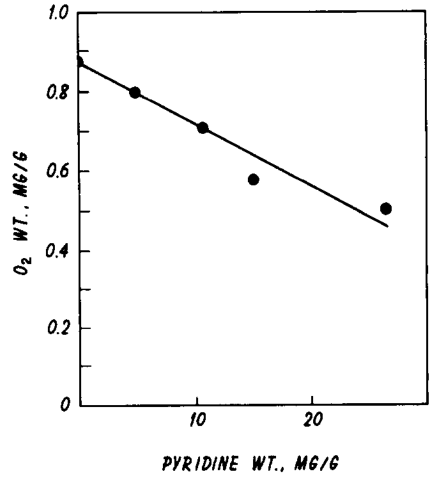

FIG. 2. Oxygen chemisorption as a function of pyridine loading on American Cyanamid catalyst.

TABLE 2

Oxygen Chemisorption on Different Catalysts

| Catalyst |  | $O_2$ chemisorption (mg/g) |  |
|---|---|---|---|
| No. | Support | Mo[a] | CoMo[b] |
| 1 | $\gamma$-$Al_2O_3$ | 0.58 | 0.76 |
| 2 | 10% $SiO_2$–$Al_2O_3$ | 0.48 | 0.70 |
| 3 | 25% $SiO_2$–$Al_2O_3$ | 0.36 | 0.59 |
| 4 | 75% $SiO_2$–$Al_2O_3$ | 0.19 | 0.36 |
| 5 | $SiO_2$ | 0.05 | 0.11 |
| 6 | 75% $SiO_2$–MgO | — | 0.47 |
| 7 | $TiO_2$ | — | 0.13 |
| 8 | 5% Zn–$Al_2O_3$[c] | — | 0.64 |
| 9 | $\gamma$-$Al_2O_3$ (+5% Zn)[d] | — | 0.63 |
| 10 | American Cyanimid | — | 0.87 |
| 11 | Topsøe | 0.97 | 0.94 |
| 12 | Ketjenfine | — | 0.64 |

[a] 8% Mo.

[b] 3% Co 8% Mo.

[c] 5% Zn impregnated on $\gamma$-$Al_2O_3$.

[d] 5% Zn impregnated on catalyst 1.

hydrogenation rate constants versus $O_2$ chemisorption for the Mo and CoMo catalysts, respectively. Triplicate runs on the CoMo catalyst 1 gave $k_T = 32.5 \pm 0.9$ cm$^3$/g min atm and $k_H = 64.2 \pm 2.8$ cm$^3$/g min atm. For both sets of catalysts, the HDS plots show curvature, whereas, the hydrogenation plots are linear. Despite the fact that the Mo catalysts were tested at a higher temperature than the CoMo cataylsts, the dramatic promotional effect of Co on HDS activity (Fig. 4A vs B) is not reflected in $O_2$ chemisorption for the two sets of catalysts. This was further confirmed by testing the Topsøe Mo catalyst at the same temperature (350°C) as the Topsøe CoMo catalyst; $k_T$ values of 1.1 and 33.5 were obtained, respectively. Thus, although $O_2$ chemisorption was the same for these two catalysts, HDS activity was greatly promoted by the presence of Co.

## DISCUSSION

The results of Fig. 1 show that sulfided, supported catalysts containing Mo or CoMo are sensitive to the chemisorption temperature used. We take the constancy in weight at −78°C to be a true indication of the $O_2$ chemisorption capacity. At higher temperatures, continued $O_2$ addition indicates slower oxidation of the sulfide phases is taking place, with possible sulfate formation. Brinen and Armstrong (*11*) have reported the presence of sulfate by ESCA on a sulfided $CoMo/Al_2O_3$ catalyst after exposure to air. Vyskocil and Tomanova (*12*) have also indicated similar difficulty with continued oxidation of sulfided catalysts using a pulse technique. Tauster and Riley (*7*) refer to a "quasi-invarient" residual uptake, possibly due to surface oxidation, which they have corrected for in their correlations.

The data of Table 2 show that the presence of cobalt does not greatly affect $O_2$ chemisorption, despite large differences in thiophene HDS activity, as seen in Figs. 4A and 5A. If $O_2$ selectively adsorbs on HDS sites, then it must be concluded that the number of these sites is not greatly affected by Co, but rather the intrinsic activity of the sites is increased, as has been proposed earlier (*2*). However, in a series of catalysts

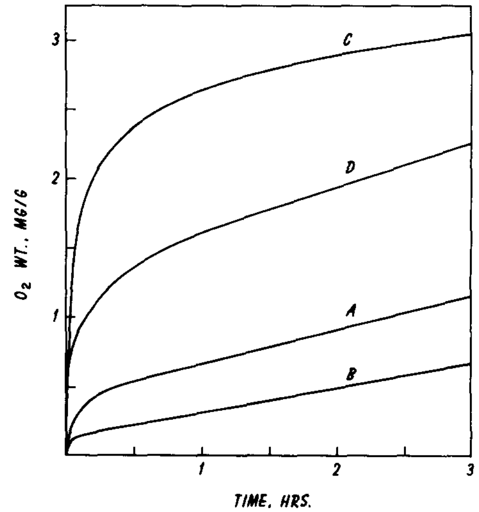

FIG. 3. Oxygen chemisorption on $Al_2O_3$ catalysts after reaction in thiophene/$H_2$. (A) $Al_2O_3$ support, (B) $Co/Al_2O_3$, (C) $Mo/Al_2O_3$, (D) $CoMo/Al_2O_3$. Weights corrected for physical adsorption of $O_2$.

having the same Co/Mo ratio, a rough correlation between HDS activity and $O_2$ chemisorption may be obtained (as indicated in Fig. 5A) if the promotional effect is the same. The appreciable scatter in Fig. 5A may be due to somewhat different promotional activity for the Co in these catalysts. A more consistent plot is obtained for the Mo catalysts in this regard. Then the $O_2$ chemisorption and catalytic activity reflect the general degree of dispersion of the active molybdenum sulfide phase. Thus, a lower dispersion would result in less HDS sites (and lower HDS activity) and a lower $O_2$ adsorption, even though the latter may not truly represent adsorption on HDS sites. A further argument against $O_2$ measuring HDS sites comes from the Zn-containing catalysts (8 and 9 of Table 2). Whether added to the support first or to the catalyst, Zn caused only about a 15% lowering in $O_2$ chemisorption compared to the catalyst without Zn (1 of Table 2), whereas, the HDS activity was drastically reduced, the more so when Zn was added to the catalyst. We may interpret this as indicating that the Zn does not radically affect the Mo dispersion, but rather poisons HDS sites or perhaps the Co-promotional effect.

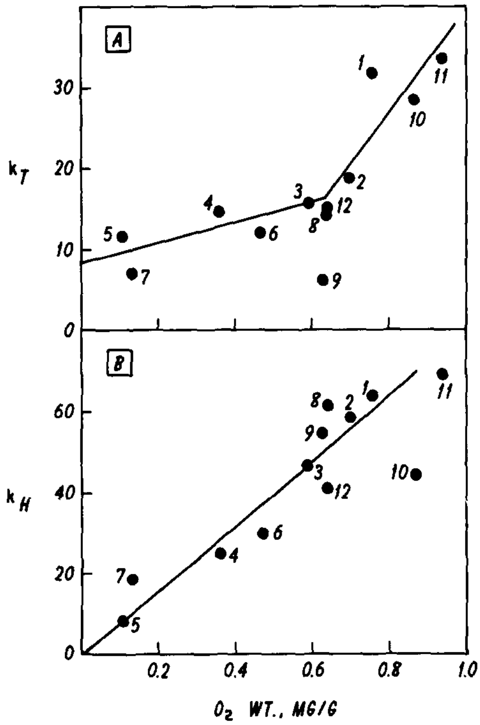

FIG. 5. Catalytic activity at 350°C of different CoMo catalysts versus $O_2$ chemisorption. Symbols same as in Fig. 4

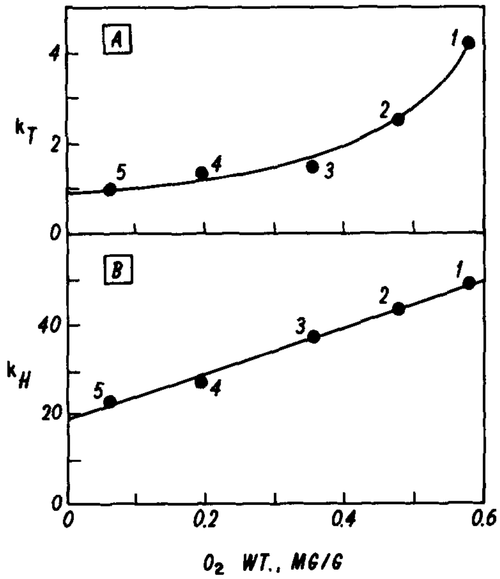

FIG. 4. Catalytic activity at 400°C of different Mo catalysts versus $O_2$ chemisorption. (A) $k_T$, rate constant for HDS, $cm^3/g$ min atm, (B) $k_H$, rate constant for hydrogenation, $cm^3/g$ min. Numbers refer to catalysts listed in Table 2.

The hydrogenation activity plots show reasonable linear correlations with $O_2$ chemisorption (Figs. 4B and 5B). Also, the Zn-containing catalysts correlate well. Only the commercial Cyanamid catalyst deviates appreciably from the correlation in Fig. 5B. One may be tempted from this to conclude that $O_2$ chemisorption is directly related to hydrogenation sites. However, the fact that the correlation for the Mo catalysts does not pass through the origin (Fig. 4B) would seem to cast doubt on this conclusion, although somewhat surprisingly, the CoMo data do extrapolate to the origin. Millman and Hall (*13*) have reported a failure of their linear $O_2$ chemisorption versus vacancy concentration plot for reduced $Mo/Al_2O_3$ catalysts to pass through the origin, which they attributed to single vacancy sites on the assumption that dual sites may be required to adsorb $O_2$. If this is the case with the sulfided catalysts, cobalt may have increased the number of dual adsorption sites at the expense of single ones. It is also possible that Mo catalysts contain two hydrogenation sites, one on which $O_2$ chemisorbs and the other which does not chemisorb $O_2$, and the presence of cobalt eliminates the latter, resulting in only the site which adsorbs $O_2$.

In view of the better correlation of hydrogenation activity with $O_2$, chemisorption appears to more closely relate to hydrogenation sites than HDS sites. If $O_2$ absorbs at edge sites, then hydrogenation sites might well be involved since Tanaka (*14*) and Voorhoeve and Stuiver (*15*) have proposed that the edge sites are active for hydrogenation. Also, Stevens and Edmonds (*6*) have proposed that basal plane sites are active for HDS. If this is correct, then with decreasing dispersion of the active phase, both HDS and hydrogenation activity would be expected to decrease, as would $O_2$ chemisorption, and a rough correlation would obtain for both catalytic functions with $O_2$ adsorption, as observed, but $O_2$ would only be adsorbed at the edge hydrogenation sites and correlate with hydrogenation activity.

It is interesting that preadsorbed pyridine decreased $O_2$ uptake. The slope of the line in Fig. 2 corresponds to about 13 molecules of pyridine adsorbed for each O chemisorption site covered (assuming one O per adsorption site). This would indicate that the major part of the pyridine adsorbs on sites inactive for $O_2$ adsorption or that $O_2$ adsorbs on only a fraction of the active sites. Since pyridine is known to be a poison for both HDS and hydrogenation activity of these catalysts (*16, 17*), we cannot distinguish whether the $O_2$ adsorbs on HDS or hydrogenation sites by this experiment. Nevetheless, the fact that $O_2$ adsorption decreases along with catalytic activities as pyridine is added implies at least an indirect relationship between $O_2$ adsorption and either HDS or hydrogenation sites, or both.

An opposite effect was observed with coke on the catalyst. Now, larger $O_2$ uptakes were obtained, and the uptake continued even at −78°C. This certainly indicates adsorption of $O_2$ on or partial oxidation of the coke, and places in doubt the general utility of this technique for assaying active sites on coked catalysts. It is interesting to note that $Co/Al_2O_3$ effectively suppressed coke formation compared to the $Al_2O_3$ support (Table 1), demonstrating the hydrogenation ability of sulfided Co; however, its effect was considerably less in the presence of Mo.

In summary, it must be concluded that no clear evidence comes from our study which establishes a direct relationship between $O_2$ chemisorption and either thiophene HDS or olefin hydrogenation sites, invalidating the technique for quantitatively measuring active sites for these reactions on sulfided catalysts. It is more probable that $O_2$ chemisorption is generally related to the state of dispersion of the active phase which is only indirectly related to active sites.

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## REFERENCES

*1.* Chung, K. S., and Massoth, F. E., *J. Catal.* **64**, 332 (1980).

*2.* Massoth, F. E., and Chung, K. S., Proc. 7th Inter. Cong. Catal., 629, Tokyo (1980).

*3.* Tauster, S. J., Pecoraro, T. A., and Chianelli, R. R., *J. Catal.* **63**, 515 (1980).

*4.* Stevens, G. C., and Edmonds, T., *J. Less Common Metals* **54**, 321 (1977).

*5.* Chianelli, R. R., and Tauster, S. J., *J. Catal.* **71**, 228 (1981).

*6.* Stevens, G. C., and Edmonds, T., *J. Catal.* **71**, 230 (1981).

*7.* Tauster, S. J., and Riley, J. L., *J. Catal.* **67**, 250 (1981).

*8*. Tauster, S. J., and Riley, J. L., *J. Catal.* **70,** 230 (1981).

*9*. Cable, T. L., Massoth, F. E., and Thomas, M. G., *Fuel Proc. Tech.* **4,** 265 (1981).

*10*. Bartholomew, C. H., private communication, manuscript in preparation.

*11*. Brinen, J. S., and Armstrong, W. D., *J. Catal.* **54,** 57 (1978).

*12*. Vyokocil, V., and Tomonova, D., *React. Kinet., Catal. Lett.* **10,** 37 (1979).

*13*. Millman, W. S., and Hall, W. K., *J. Catal.* **59,** 311 (1979).

*14*. Tanaka, K., and Okuhura, T., *Catal. Rev. Sci. Eng.* **15,** 249 (1977).

*15*. Voorhoeve, R. J. H., and Stuiver, J. C. M., *J. Catal.* **23,** 228 (1971).

*16*. Desikan, P., and Amberg, C. H., *Canad. J. Chem.* **42,** 843 (1964).

*17*. Cowley, S. W., and Massoth, F. E., *J. Catal.* **51,** 291 (1978).