

Aluminum Inclusions and Precipitates in Restacked Exfoliated MoS₂

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Exfoliated MoS₂ (separated into single monomolecular layers suspended in solution) is restacked with aluminum ions available. Results suggest that the ions can be "included" as a monolayer between the MoS₂ layers, precipitated as Al(OH)₃, or present as AlO₂⁻ ions (presumably sodium aluminate). X-ray diffraction measurements are reported to distinguish among the various forms. pH variations during the flocculation and drying vary the X-ray pattern. Surprisingly it is found that the "inclusion" method (rather than a "coprecipitation" method) seems to yield a catalyst with a higher surface area (CO₂ adsorption), a higher active area (CO adsorption), and a higher catalytic activity for our test reaction, methanation. © 1988 Academic Press, Inc.

1. INTRODUCTION

As described in earlier contributions (1–4), we have been studying the exfoliation of molybdenum sulfide and studying the properties and reactions of the exfoliated material. By exfoliation we mean separating the layer compound into single molecular layers suspended in solution. The steps for exfoliating molybdenum sulfide include first intercalation with lithium and then immersion in aqueous solution with suitable agitation. The intercalated lithium reacts with the water, generating hydrogen which expands between the layers and separates the layers. As described in Refs. (1–4), the layers remain separated from each other in the suspension because OH⁻ adsorption leads to charged layers and consequently forms repulsive double layers. While the molybdenum sulfide is in suspension, species from the solution can be adsorbed on the surface and molybdenum sulfide restacked leading to what we have referred to (2) as inclusion compounds. Alternatively materials in solution can be precipitated onto the layers in suspension and the layers can be restacked leading to a condition where the layers are separated by these large precipitated particles. We have also described (3,

4) the utilization of these exfoliated materials in catalysis and indicated how very high activity can be obtained.

In our catalytic studies (4) the exfoliated material as single layers was deposited on alumina to induce a high activity. However, it was considered of interest to study the introduction of alumina by inclusion or by the deposition of aluminum precipitates in the MoS₂ lattice.

The precipitation onto our catalyst of aluminum hydroxide, with subsequent dehydration, was considered to have a potential advantage because our system is somewhat unique. Normally the catalyst is introduced from solution, and coprecipitation of the support and the catalyst leads to the burial of much of the catalyst within the solid support, not accessible to the reactants. Thus, the precipitated support approach is not favored (5). In our case, however, the catalyst is introduced in the form of solid single molecular layers, so if the support is precipitated on these layers, forming ultrafine particles, later dehydration can lead to a very large density of Mo surface sites per gram, in principle larger than could be obtained by interacting the suspended MoS₂ with suspended Al₂O₃ particles as was done in the earlier contribution (4).

TABLE 1
 Flocculation Parameters with Exfoliated MoS₂ Suspension Mixed
 with Al(NO₃)₃ Solution

Expt. No.	pH of MoS ₂ Suspension	Mixture A/B (cc)	pH of Al Solution	pH of mixture	Al/Mo
1	6.2	20/100	3.0	3.1	0.06
2	6.2	20/100	3.5	3.4	0.18
3	6.2	20/100	3.9	4.1	0.51
4	6.2	20/100	4.5	4.5	0.78
5	8.5	10/100	4.1	4.9	0.98
6	11.8	5/100	4.5	4	0.87
7	11.6	A/C = 20/100	13.2	12.4	1.5

Note. Suspension A: 1 g MoS₂ in 200 cc H₂O, washed, pH 6.2; solution B: 0.1 M Al(NO₃)₃, pH raised as indicated using NaOH; solution C: 0.1 M NaAlO₂.

This contribution reports such experiments with aluminum. The ultimate objective of the research is, of course, primarily focused in the direction of utilization of these configurations in catalysis. However, the interaction of aluminum ions with the MoS₂, emphasized here, has turned out to be a very interesting study in its own right.

2. EXPERIMENTAL

2.1. Sample Preparation

In most cases reported, the molybdenum disulfide was exfoliated in aqueous solution in one container, and aluminum nitrate or sodium *meta*-aluminate was dissolved to form an aqueous solution in another container. The aluminum nitrate solution initially had a pH on the order of 3, and sodium hydroxide was normally used to raise the pH to a higher value. The increase in pH can be attained only by an extremely slow addition of the base. The aluminum solution and the MoS₂ suspension were then mixed. Before mixing, the pH of the MoS₂ suspension was adjusted (usually to pH 6.2). When pH adjustments were desired, nitric acid or sodium hydroxide was used. After mixing, the flocculated molybdenum sulfide was washed three times (to remove soluble compounds from the flocculated surfaces).

Table 1 shows the pH and the concentra-

tions used in the suspensions and solutions for these experiments. In samples 1–5, it was our object to produce inclusion compounds. In sample 6, it was our object to induce precipitation, so as to trap particles of Al(OH)₃ between the MoS₂ layers. The difference between the two groups was the pH chosen for the molybdenum sulfide in suspension. In the first group the pH was close to neutral to avoid excessive precipitation of the aluminum ion. Then the aluminum would tend to adsorb onto the single layers of molybdenum sulfide rather than form precipitated particles. On the other hand, when the precipitated particles were desired as in sample 6 the pH of the molybdenum sulfide suspension was made high to induce Al(OH)₃ precipitation as the liquids were mixed and before adsorption of Al ions onto the MoS₂. In the case of sample 7, both solutions were basic (Al was introduced as NaAlO₂). In all cases upon mixing, flocculation occurred rapidly, but in the presence of AlO₂⁻ flocculation was much faster. The materials used in exfoliation are described in Refs. (1–4).

2.2. X-Ray and SEM Measurements

The results of the experiments were studied with X-ray diffraction as the primary tool. Measurements were made with Ni-filtered CuK α radiation using a Philips

diffractometer. An electron microprobe attachment to the scanning electron microscope was used to determine the ratio of aluminum to molybdenum in the final product, as is also indicated in Table 1.

2.3. TPD and Catalysis Measurements

Temperature-programmed desorption (TPD) (3) and catalytic measurements of our test reaction methanation (4) were made to determine how the samples prepared with "coprecipitated" or included aluminium are compared to each other and to the samples discussed in an earlier report (3). In the TPD measurements, the samples were first reduced at 550°C in CO for approximately 2 h and then cooled under vacuum to room temperature. Then TPD measurements on CO, O₂, or CO₂ were made. For each case, the excess gas was introduced at 100 Torr pressure for 20 min at room temperature and then evacuated. The temperature was increased to 300°C and the desorption peak was observed on a quadrupole mass spectrometer. The integrated amount of desorption provided an indication of active site density. The results are shown in Fig. 7 and discussed in Section 3.2.

The catalytic activities for methanation reaction (4), using a H₂:CO ratio of 5:1 with a total flow of 30 ml/min at 1 atm, were measured with a flow-through reactor with no circulation and the products were measured using a Varian gas chromatograph with a 13X molecular sieve and a Porapak N column in series. The result is represented in Fig. 8 and also discussed in Section 3.2.

3. RESULTS

3.1. X-Ray

Figure 1a shows the X-ray diffraction spectrum of as-received unexfoliated MoS₂

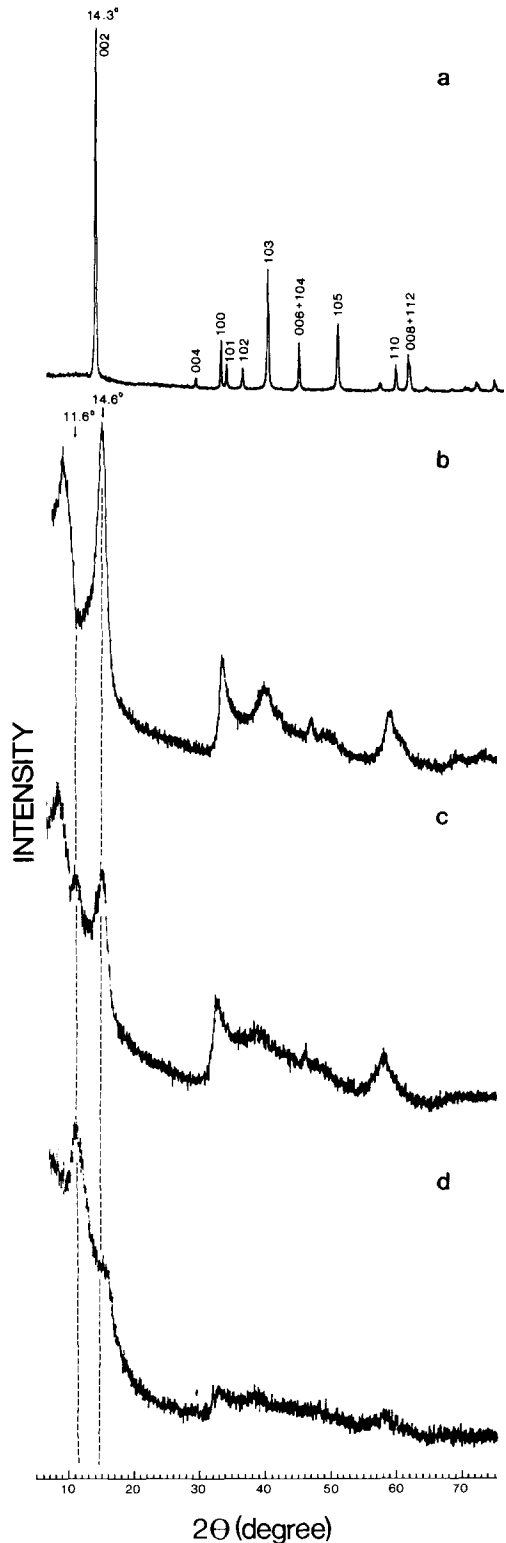


FIG. 1. X-ray diffraction patterns: (a) as received unexfoliated MoS₂ with the (002) line at 14.3°. (b, c, d) The patterns for samples with (Al:Mo) ratios of 0.06, 0.51, and 0.98, respectively. The peak at 8° is due to the sample holder.

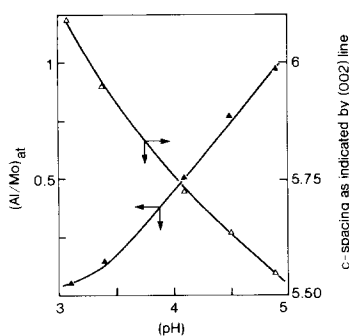


FIG. 2. Variation of (Al:Mo) ratios with the pH of the $\text{Al}(\text{NO}_3)_3$ solution. As this ratio increases the spacing along the c -axis, corresponding to (002) lines, decreases.

with the (002) line at about 14.3° , Fig. 1b the pattern for sample 1 (Table 1), Figure 1c the pattern for sample 3, and Fig. 1d the pattern for sample 5. It is observed when these figures are compared that the intensity of the (002) line decreases and that of the line at 11.6° increases with the increasing percentage of aluminum included. The peak at 8° is associated with a sample holder that was used at certain times. When a plexiglass sample holder was used the 8° peak disappeared.

Figures 2 and 3 summarize the results from samples 1 to 5. Figure 2 shows the variation of the Al:Mo ratio with pH. As the pH increases from 3 to 4.5, more aluminum is deposited; the Al:Mo ratio in-

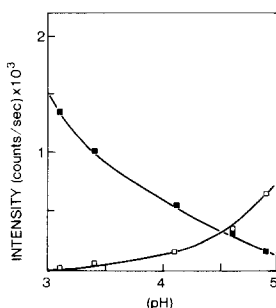


FIG. 3. Variation of the intensity of (002) line at 14.6° with the pH of the $\text{Al}(\text{NO}_3)_3$ solution. With an increase in the pH, the intensity of the MoS_2 (002) line at 14.6° decreases (■) and that of the line at 11.6° increases (□).

creases from 0.06 to 0.98. Figure 2 also indicates that as the Al:Mo ratio increases the (002) line shifts toward higher angles. Apparently the c -spacing decreases, indicating a contraction of the lattice as aluminum is added. Figure 3 indicates that the peak height at 11.6° increases and the peak due to the (002) line decreases, with an increasing aluminum-to-molybdenum ratio.

Figure 4 shows results for sample 6 where the sample was heated to ever increasing temperatures to dehydrate the aluminum hydroxide. Figure 4a shows the results where the sample is only heated to 70°C (the same temperature as that of the samples of Fig. 2) and the picture looks substantially different from those of Figs. 1a–1d. First, Fig. 4a shows a sawtooth pattern, typical of a single-layer formation (1, 8) with (100) and (110) lines representing the reflections from planes of MoS_2 layers perpendicular to the c -axis, while the (002) line indicates the reflections along the c -direction. The appearance of the (002) line at 15° indicates that a part of the sample is periodic in the c -direction because a perfectly prepared single-layer sample (8) has no “ c -spacing” and consequently all (00 l) lines, particularly the (002) line, are absent. Second, there is an extra line at 7.55° , in addition to the line at 15° . Due to the fact that the d -spacing of the line at 7.55° (11.86 \AA) is almost twice the d -spacing of the line at 15° (5.91 \AA), we have assigned an index of (001) to the line at 7.55° . This means that the lattice in sample 6 is expanded by a factor of 2 in spacing (relative to the 2H-MoS_2 (Fig. 1a) or to the exfoliated restacked MoS_2) as a result of aluminum hydroxide precipitation.

As the sample is heated to higher temperatures the two lines at 7.55° and 15° disappear to be replaced by a line at 11.6° . Figure 4b shows the results after heating the sample at 305°C for 48 h in air. Figure 4c shows the results after heating it to 350°C in air, where it is seen that the 11.6° line has taken over completely. Figure 5 shows a plot of the amplitude of the 15° line compared to

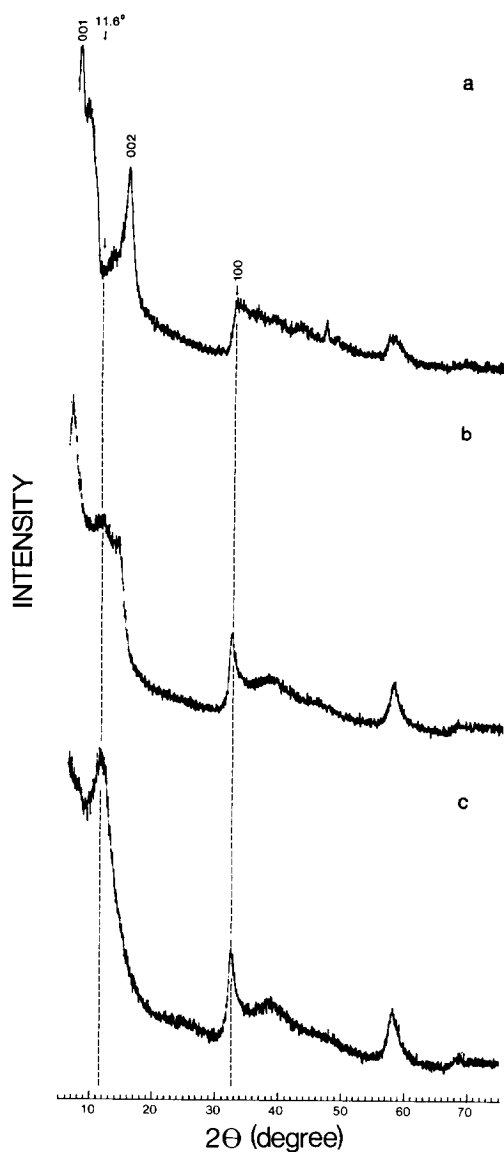


FIG. 4. X-ray diffraction pattern for a sample heat treated at varying temperatures: (a) 70°C, (b) 220°C, and (c) 305°C. Note that this severe temperature treatment does not affect the (100) lines of these samples. The peak at 8° is due to the sample holder and the (110) peak shows at 58.4°.

the amplitude of the 11.6° line as the annealing temperature is raised. It is remarkable (see Fig. 4) that the (100) line is essentially unchanged by all these temperature treatments, whereas the (002) line at 15° disappears completely and is replaced by a new line at 11.6°.

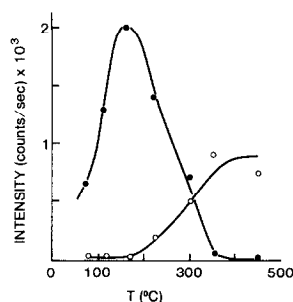


FIG. 5. Temperature variation of the intensity of the (002) line at 14.6° (■) and that of the line at 11.6° (□).

In the preparation of sample 7 (see Table 1) both the molybdenum sulfide and the aluminum were prepared in a highly basic solution. The molybdenum sulfide pH was left unchanged after exfoliation (this means that a reasonably high concentration of lithium hydroxide was present in that solution), and the pH of the dissolved sodium *meta*-aluminate was also left unchanged. When the two solutions were mixed there was instantaneous flocculation of the molybdenum sulfide. The variation of the X-ray diffraction pattern for a sample thus prepared is shown as a function of heat treatment in Fig. 6. From left to right on the abscissa of Fig. 6 the numbers indicate various 2-h steps in drying, described in the figure.

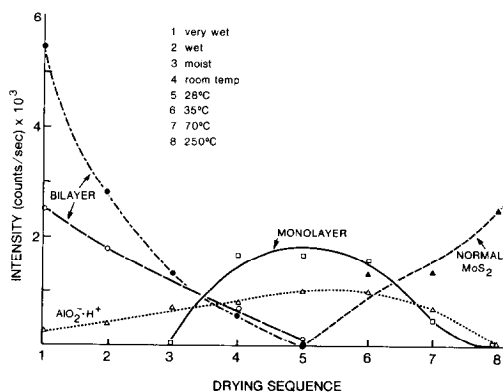


FIG. 6. Intensity variation of different peaks for the $\text{MoS}_2\text{-NaAlO}_2$ system as the slurry is dried. For drying procedure, see text. Peaks correspond to 7.5° (11.83 Å) (●), 9.6° (9.25 Å) (□), 11.6° (7.65 Å) (△), 14.3° (6.21 Å) (▲), and 14.6° (6.10 Å) (○).

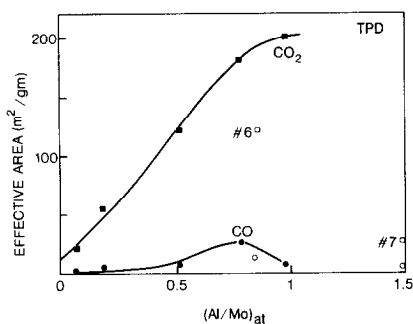


FIG. 7. Effective surface area for adsorption of CO and CO₂ for some of the samples shown in Table 1. The CO₂ adsorption at room temperature reaches a constant value indicating the total surface area of samples. The CO adsorption represents how catalytically active these samples are. Samples 6 and 7, prepared at high pH values, do not follow the trend.

Thus, from left to right, the amount of moisture in the sample decreases steadily. The results with the wet sample can be explained in terms of water entrapped between the MoS₂ layers (6). The peak at 7.55° corresponds to two molecules of water entrapped between each of the layers of MoS₂. As the sample is dried these peaks disappear. First they are replaced by a peak at 9.6° that corresponds to one layer of water (7) between the layers of MoS₂ and then as the sample is heated further this peak also disappears, the residual peak being the normal 14.3° peak of restacked molybdenum sulfide with no inclusions. There is a constant peak at 11.6° which does not change with drying.

3.2. TPD and Catalytic Activity

As discussed in Ref. (3), the CO₂ desorption peak seems to reflect well the total surface area of the sample prepared from alumina-supported molybdenum sulfide.

The large surface area registered in Fig. 7 by samples 4 and 5 (black squares) is surprising, considering that, according to the discussion above, the aluminum is supposed to be "included"—buried between the MoS₂ layers. The results indicate that by the time the TPD measurement is made

the MoS₂ layers must be broken up by one of the various treatments it has undergone. It could disintegrate during the dehydration of the inclusions or during the mild oxidation treatment received while making a TPD run for oxygen adsorption. It was not determined which step caused the disintegration. But it is clear that most of the atoms in the sample were accessible for CO₂ adsorption.

Samples 6 and 7 showed CO₂ adsorption consistent with that of the models of the preceding section. Sample 6 showed a lower surface area presumably because much of the alumina is in the form of crystallites formed by Al(OH)₃ precipitation during the preparation of the mixture. Sample 7 showed a very low surface area presumably because the solution sodium *meta*-aluminate is leached out from the MoS₂ particles during the drying process.

The oxygen TPD measurements are not shown, because they showed no consistency. It has been found in more recent experiments that the "surface coverage" of oxygen as measured by TPD depends sensitively on the length of the initial CO reduction, becoming very large (35 m²/g) with overnight reduction on a sample equivalent to sample 5. Because the exact length of the reduction was not considered an important variable when these measurements were made, there was considerable scatter in the "surface coverage of oxygen."

4. DISCUSSION

4.1. X-Ray and TPD Results

The most interesting feature of these formulations is the appearance of a diffraction line at about 11.6°. We believe that the line is associated with the ion AlO₂⁻ separating the MoS₂ layers. The line then indicates a new *c*-spacing of the molybdenum sulfide when the AlO₂H or AlO₂Na is "included." The arguments are as follows.

We have not identified such a line with any of the simple formulations of aluminum hydroxide, boehmite, α -alumina, sodium *meta*-aluminate, or Al-free MoS₂.

In Figs. 4a–4c it is noted that the (100) line is unchanged with heat treatment, suggesting that the molybdenum sulfide layers are still present and unaffected by the heat treatment used. However, the (002) line of the MoS₂, reflecting the *c*-spacing, decreases while the 11.6° line correspondingly increases in intensity (see Fig. 5). The correspondence between the increase in the 11.6° line and the decrease in the (002) line is observed not only in Fig. 5 but also in Fig. 3. Again, noting the scale of Figs. 1a–1d, the (100) line is to a great extent unchanged while the (002) line disappears and the 11.6 line grows. Thus it appears that the MoS₂ layers are unchanged, but an increasing fraction of the sample is represented by a *c*-spacing associated with the 11.6° line (7.65 Å). Because from Fig. 3 the appearance of the 11.6° line corresponds to more Al, we attribute the lattice expansion to a uniform layer of an aluminum compound between the MoS₂ layers.

The heat treatment (Fig. 5) leading to the appearance of the 11.6° line provides further evidence that the line is associated with the AlO₂⁻. Aluminum hydroxide is known to dehydrate to boehmite (AlOOH) at temperatures on the order of 190°C (9), whereas it requires on the order of 500°C to convert to γ -alumina. In the results of Fig. 5 it is seen that the 11.6° line appears with a 200°C treatment and is well established after 350°C treatment, indicating dehydration only to the layer compound boehmite.

In the results of Fig. 4, where the pH was adjusted to induce the precipitation of Al(OH)₃, the appearance of what we have termed a (001) line suggests that for some parts of the flocculated molybdenum sulfide there is a uniform wide expansion, almost to double the Mo–Mo spacing. This expansion of the lattice could be due, perhaps, to water, LiOH, or some highly hydrous oxide (7). With heat treatment these lines do not shift in angle (the spacing remains constant) but lower in intensity (the fraction of MoS₂ with the spacing decreases with heat treatment). The 11.6° line correspondingly in-

creases, suggesting dehydration to AlO₂⁻. The sawtooth shape of the pattern in Fig. 4a indicates that a large percentage of the molybdenum sulfide is in the single-layer form, presumably separated by precipitated particles of aluminum hydroxide. When the sample is heated the single-layer configuration disappears rapidly: by 165°C the final shape of the (100) line (Fig. 4b) has already appeared. The dehydration of the adsorbed aluminum hydroxide that leads to the peak at 11.6° requires more heat.

A particularly interesting observation is that using the preparation method of Fig. 1 where the solution is always acid, the aluminum adsorbs immediately as AlO₂⁻ (if we assume our interpretation is correct and the 11.6° line is associated with the adsorption of this species). This adsorption in the basic form, presumably as AlOOH, means an extremely strong attraction between the AlO₂⁻ molecule and the molybdenum sulfide layer. It seems that the Al–Mo interaction is strong enough to dissociate any tendency toward “polymer” formation (10, 11) of the Al(OH)_{*n*}^{3-*n*} group in solution as pH values approach 5. By the simplest James–Healy model (12) for adsorption, Al(OH)₂⁺, which combines with an adsorbed OH⁻ to form Al(OH)₃, could be expected for this low-pH flocculation. The phase that leads to a line at 11.6° is highly stable. We have tested it up to 600°C. Calcining in oxygen, however, destroys the line, as expected because the MoS₂ will convert to MoO₃.

The results of Fig. 6 are somewhat surprising, because the 11.6° line does not dominate the X-ray pattern. There is a small 11.6° peak but except for this there appears to be no aluminum between the MoS₂ layers upon heating up to 250°C. This is suggested because there is no shift in the *c*-spacing from as-received MoS₂. And yet the Al:Mo atomic ratio is found to be on the order of 1.5. We suggest that the aluminum is adsorbed initially on the layers, causing the rapid flocculation, perhaps as NaAl(OH)₄ because of the very high pH in the solution. But the lack of any indication

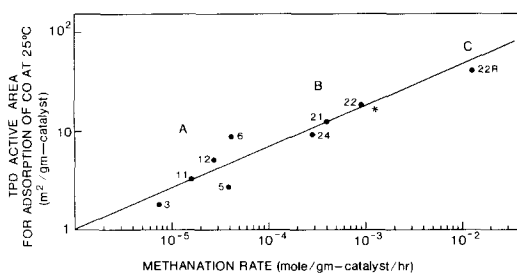


FIG. 8. Comparison of catalytic activity of sample 4 for production of methane (*) with previously reported samples in Ref. (4). Group A indicates the activity of various preparations of $\text{MoS}_2\text{-Al}_2\text{O}_3$ with no promoter. Group B shows the activity of $\text{MoS}_2\text{-Al}_2\text{O}_3$ with Ni promoter. Note that the activity of our current sample 4, with no Ni present, is comparable with the Ni-promoted samples of group B.

of aluminum being present between the layers after the 250°C treatment (no shift in the (002) line) suggests that this soluble form of the aluminum has been leached out to the surface of the MoS_2 particles as the water was removed from the sample. This hypothesis has been checked by washing the dried restacked MoS_2 in a basic solution and finding that the Al:Mo ratio becomes negligible, despite its initial 1.5 value. Such a model is also reasonably consistent with the very low surface area from CO_2 adsorption observed in this case. As the MoS_2 without the alumina would simply be the restacked MoS_2 with its normal low surface area, the observed surface area suggests separated MoS_2 and Al_2O_3 phases.

4.2. Catalysis Results

The TPD results for CO showed a high adsorption for samples with aluminum in the form of inclusion. Sample 4 was observed to have the highest value of CO "surface coverage" of any sample we have studied with no promoter. Thus the measurement of methanation (hydrogenation of CO) activity was made to compare sample 4 with those reported earlier. The sample was treated as the earlier sample, featuring calcination followed by reduction in H_2 at 550°C for activation. In Fig. 8, a compari-

son of the results with those of Ref. (4) shows consistency with the result of Fig. 3 of that article. In that series it was concluded that the methanation activity increases with the square of the CO adsorption as measured by TPD. As sample 4 has the highest CO adsorption capacity of any of the nonpromoted MoS_2 samples, the rate observed here, 1.5×10^{-3} mole/(g-catalyst/h) at 300°C, is higher than those reported in Ref. (4) for nonpromoted catalysts.

5. CONCLUSIONS

The appearance of an X-ray diffraction peak at about 11.6° suggests a new c -spacing for MoS_2 with some form of aluminum ion present. If the aluminum is added under conditions (low pH) where it should be adsorbed rather than precipitated, the 11.6° line appears and its intensity is related to the concentration of aluminum. If the aluminum is added in such a way that it should be precipitated as $\text{Al}(\text{OH})_3$, the 11.6° line forms but only upon heating for dehydration. Because the line is stable up to 500°C and because its magnitude increases as the normal (002) line of MoS_2 at 14.6° decreases, we suggest that it is the stable AlO_2^- form of alumina, "included" as a monolayer, that causes the c -spacing of MoS_2 to increase.

Using various techniques, we find that MoS_2 "supported" on alumina can be prepared to show a very high surface area, as measured by TPD, and a high catalytic activity as measured by our test reaction, methanation. The results are quite different from that expected, where we anticipated that the most active samples would be those with fine crystallites of alumina, produced by precipitation, able to support the MoS_2 in the classical way. However, it was found that the most active samples are those that are prepared by "inclusion" methods where the aluminum oxide is in the AlO_2^- monolayer form between the MoS_2 layers, corresponding to the presence of a high-intensity 11.6° line. Samples featuring this line show a high surface area and

catalytic activity after normal processing, the normal processing apparently breaking down the MoS₂ layers into small fragments.

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