JOURNAL OF CATALYSIS **103**, 334–345 (1987)

High Activity Catalyst from Exfoliated MoS_2

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Received May 14, 1986; revised September 10, 1986

By using exfoliated MoS_2 suspended as single layers in solution we have been able to prepare what appear to be unusually high activity catalysts, where hydrogenation of CO, methanation, was used as the model reaction. The process depends on three features in the preparation; first, the preparation of the single molecular layer MoS_2; second, the deposition of these as single layers onto high-surface-area Al_2O_3 (or rather deposition of Al_2O_3 onto single layers of MoS_2); and third, the deposition of monolayers of nickel onto the single layers of MoS_2. With this structure, suitably calcined and reduced to improve the interaction between the Mo, the Ni, and the Al_2O_3, we have a very high density of active sites per unit area (and per unit mass). The most active sites appear to be a form of oxysulfide. The active sites when nickel is present behave differently from Ni supported on Al_2O_3. The $Ni/Mo/Al_2O_3$ composition yields CO_2 as the by-product of methanation, instead of the H_2O observed with the Ni/Al_2O_3 composition, and has a different activation energy. A specific formulation designed to give the maximum density of accessible $Ni/Mo/Al_2O_3$ sites shows an activity substantially higher than Ni/Al_2O_3. For formulation without Ni the activity of catalysts prepared by exfoliation shows substantially higher activity than those prepared by precipitation from ammonium heptamolybdate.

1. INTRODUCTION

Molybdenum disulfide in its various forms is of great interest in several catalytic reactions. The most important of these reactions is hydrodesulfurization (*1–10*), although other reactions are also important. For example, it is useful for hydrogenation in recovery of sulfur-containing heavy oils. A third area of possible interest in the use of MoS_2 is in methanation (*11–14*) and water–gas shift (*15–19*) reaction. In our work to be described we have emphasized methanation as a simple model catalytic reaction for testing and comparing the activity of MoS_2-based catalysts.

We have recently introduced the techniques of MoS_2 exfoliation and of inclusion of metal ions into MoS_2 (*20, 21*). By exfoliation we mean the separation of MoS_2 into individual molecular planes, single-layer platelets in suspension in aqueous or other solutions. By inclusion we mean the adsorption of ions onto these single layers and reforming the single layers with the included species between the molecular layers, forming essentially a new compound. In addition, we have described temperature programmed desorption (TPD) studies of MoS_2 in various formulations (*22*). The results from the peak heights and the peak temperatures in TPD studies of CO, CO_2, and O_2 suggest that one can obtain a reasonable picture of the active sites (both the basal and edge) on MoS_2.

In the present contribution we discuss efforts to take advantage of these formulation techniques and measurement methods to prepare a combination of molybdenum sulfide, alumina, and appropriate promoters to provide catalysts of unusually high activity.

2. PROCESSING MoS_2

In order to indicate what options we have in trying to formulate active MoS_2, a minimal discussion of exfoliation and inclusion must be introduced, despite the fact that it has been described in detail in earlier reports (*20, 21*).

0021-9517/87 $3.00

2.1. *Exfoliation*

There are several steps in the exfoliation of MoS_2 into single layers. We start with MoS_2 powder from the Materials Research Corp. The MoS_2 is soaked in a solution of *n*-butyllithium in hexane under an argon atmosphere in a glove box for several hours to days. This is a well-known procedure (*23*) to intercalate lithium in between the layers of MoS_2. The MoS_2 is then introduced into an aqueous solution, where the water reacts with the intercalated lithium, and hydrogen is generated. The hydrogen gas between the MoS_2 layers "explodes" the crystallites into single layers suspended in the aqueous solution. If the aqueous solution has a pH greater than about 2 the MoS_2 will remain suspended and not flocculate.

2.2. *Inclusion*

The MoS_2 can be recrystallized with "inclusions" foreign species between the MoS_2 layers (*21*). In accordance with reasonably well understood models (*24*), if the pH of a metal nitrate solution is raised but not quite to the point of precipitation as the hydroxide, the cation will adsorb as a monolayer on the solid suspended in this solution. Thus, if we introduce such a cation into the suspended aqueous solution of MoS_2, or if we exfoliate in a solution of the salt (we usually use nitrates), then if the pH is adjusted the cations can and will deposit as a monomolecular layer on the single layer platelets of MoS_2. This has been shown to occur with exfoliated MoS_2 by X-ray diffraction measurements. It is found that the deposition of cobalt or nickel hydroxide on the molybdenum disulfide causes a uniform shrinking of the *c*-spacing in the lattice when the MoS_2 is reconstructured by flocculation or centrifuging. The deposition of lead as an inclusion material on the other hand causes an expansion of the MoS_2 lattice in the *c*-direction.

It is also found with many of the inclusion compounds that the presence of the metal cations induces flocculation at pH values where flocculation does not occur with molybdenum disulfide alone. This flocculation could be due either to the extra ionic charge associated with the multivalent cations (multivalent cations are known to induce flocculation (*25*)) or it could be associated with the lowering of the double-layer repulsion between the single-layer molybdenum sulfide platelets due to the adsorption of the hydroxylated cations.

2.3. *Flocculation with Alumina*

Another means of flocculating the MoS_2 is by introducing alumina powder into the suspension. When alumina powder is present, flocculation will occur at most values of pH. The flocculation is considered to be due to an interaction between the alumina and the MoS_2. We conclude that the MoS_2 deposits on the alumina powder, depositing as single layers. There are two reasons to assume single layer deposition: First, as the MoS_2 will not flocculate onto itself at an intermediate pH, it is reasonable to believe that it will not flocculate onto another single layer MoS_2 that coats an alumina particle. Second, we find that within a factor of 2 the amount of MoS_2 which can be taken up by 1-μm diameter alumina powder corresponds to the surface area of the powder. Specifically, 1-μm powder will clear a solution with 2 wt% MoS_2 but will not clear a solution with 5 wt% MoS_2. The conclusion that single-layer coatings are obtained is of great interest in the formulation of active catalysts.

Flocculation of the MoS_2 at intermediate pH also occurs if the suspension initially is at pH 3 or 4 with aluminum nitrate in solution and the MoS_2 in suspension, and the pH is raised to a value such that the aluminum hydroxide tends to precipitate (formation of alumina inclusion). Such an approach makes the much finer aluminum oxide powders to be deposited on the surface of the MoS_2.

2.4. *Desired Configuration*

The desired configuration for high cata-

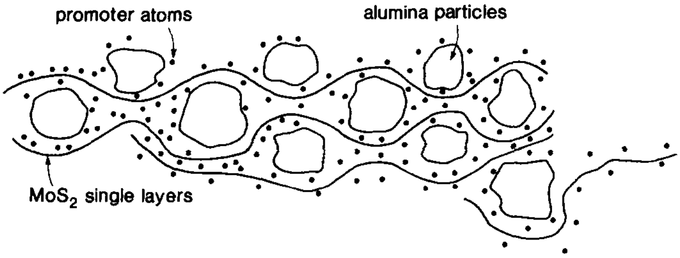


FIG. 1. The possible cross-sectional configuration of MoS_2 single layers on Al_2O_3 with Ni promoters in between. Simultaneous flocculation occurs when an Al_2O_3 suspension in a nickel nitrate solution at pH 6.2 is mixed with a suspension of MoS_2 single layers in water at the same pH.

lytic activity, or the configuration we have been attempting to formulate, using the above techniques for processing the MoS_2 catalyst, is as follows. In accordance with the views of Topsøe (*26–28*), we would like to form single layers of MoS_2 supported on Al_2O_3, with monolayers of Ni promoter deposited on the MoS_2. In forming an inclusion compound, we have concluded above that one monolayer of promoter is deposited on the surface of the MoS_2 single layers. At the same time we have concluded that flocculation of the MoS_2 occurs as single layers on the surface of alumina. Of course, our studies of coating the alumina with MoS_2 were done with 1-μm Al_2O_3 because the MoS_2 platelets are of that order of diameter. For high surface area we want fine alumina, and in this case we want the alumina to deposit on the single layers of MoS_2. And, as suggested, we want monolayers of promoter on the MoS_2 as well.

The goal of the research thus was to obtain a configuration something like that of Fig. 1. We have found (*22*) that with flocculation of the MoS_2 onto fine particles of an oxide the BET area of the material increases to a very high level compared to either the BET area of the oxide or of the as-received MoS_2. Thus, we believe that the presence of particulate matter that is deposited between the layers of the MoS_2 as in Fig. 1 allows easy access of gases to the total surface of the MoS_2. On the other hand, for highest dispersion of nickel onto this surface we want essentially to produce an inclusion compound, where that is deposited onto the particles of alumina as indicated in Fig. 1.

Following the preparation of the catalyst in this configuration, calcination, sulfidation, or reduction can be used to improve the interaction between the alumina, the Mo, and the promoter metal.

There are difficulties in depositing both the nickel and the alumina together because either the presence of the nickel or the presence of the alumina will induce flocculation. Thus, obtaining both at the same time in the right proportion is difficult. Most of the studies below are studies of molybdenum disulfide on alumina with no promoter designed to determine the optimum fraction of MoS_2 on a support of fine Al_2O_3 (about 300 Å in diameter).

3. RESULTS WITH VARIOUS FORMULATIONS

3.1. Sample Preparation

In Tables 1–3 the 28 samples used in this series, including oxides and blank samples, are listed. Samples prepared using exfoliation are compared to samples prepared by precipitation from ammonium heptamolybdate (AHM), and also are compared to two commercial catalysts.

For a practical comparison, the conversion rate is expressed in mole/g/hr. The BET areas are given for many of the formulations and also the areas measured by CO adsorption will be indicated later (Fig. 3), so that if of interest, the rates can be converted to mole/cm^2/hr.

TABLE 1

Methanation Rate for Various Catalysts, Calcined at 500°C

Sample No.	Composition (wt%)			BET surface area (m^2/g)	Rate after 20 hr (mole/g-catalyst/hr)	
	MoS_2[a]	Exfoliated MoS_2	Al_2O_3		400°C	300°C
1	100			6.6	2.6×10^{-4}	2.8×10^{-5}
2		100		0.9	2.2×10^{-5}	2.5×10^{-6}
3		85	15	32	6.3×10^{-5}	7.5×10^{-6}
4		70	30		1.6×10^{-4}	1.9×10^{-5}
5		50	50	42	3.3×10^{-4}	3.9×10^{-5}
6		30	70	73	3.5×10^{-3}	4.1×10^{-5}
7		20	80	70	1.3×10^{-3}	1.5×10^{-5}
8		15	85		7.8×10^{-4}	9.1×10^{-5}
9		10	90	62	4.1×10^{-5}	4.8×10^{-6}
10			100	72	3.2×10^{-7}	

[a] As received.

In samples 2–9 the molybdenum disulfide was exfoliated in a suspension of aluminum oxide particles of diameter 300 Å, as indicated by the supplier (Cabot Corp., Alon-γ alumina), and as measured by a scanning electron microscope. Exfoliation in all cases was done during ultrasonic agitation of the suspension. In the case of sample 5 the suspension flocculated completely. The suspensions of 2–4 and 6–9 did not flocculate completely. Consequently these samples were centrifuged a few minutes after exfoliation. Samples 6–9 were prepared to optimize the concentration of exfoliated molybdenum disulfide deposited on the alumina. These samples can be compared to samples 11 and 12 where the molybdenum was precipitated in the "classical" way from AHM onto the same Al_2O_3 powder to simulate a commercial catalyst with no pro-

TABLE 2

Methanation Rate for Various Catalysts, Calcined at 500°C

Sample No.	Composition (wt%)							BET surface area (m^2/g)	Rate after 20 hr (mole/g-catalyst/hr)	
	Al_2O_3	AHM[a]	AHMS[b]	MoO_3	MoO_2[c]	Mo[d]	Ni		400°C	300°C
11	70	30						7.3	1.3×10^{-4}	1.6×10^{-5}
12	70		30					6.7	2.7×10^{-4}	2.6×10^{-5}
13	70			30				6.8	1.1×10^{-4}	1.3×10^{-5}
14				100				2.2	1.6×10^{-4}	2.1×10^{-5}
15					?				4.4×10^{-4}	5.4×10^{-5}
16						100		1.3	5.6×10^{-4}	4.7×10^{-5}
17	97						3	41	7.2×10^{-3}	2.1×10^{-4}
18	70						30	86	[e]	3.9×10^{-3}

[a] Ammonium heptamolybdate.

[b] Sulfided ammonium heptamolybdate.

[c] Reduced sample #14 (mixed phase).

[d] Molybdenum black.

[e] High production rate, 80% CO conversion.

TABLE 3

Methanation Rate for Various Catalysts, Calcined at 500°C

Sample No.	Composition (wt%)					BET surface area (m^2/g)	Rate after 20 hr (mole/g-catalyst/hr)	
	Exfoliated MoS_2	Al_2O_3	MoO_3	Ni	Co		400°C	300°C
19	97			3			5.1×10^{-3}	6.3×10^{-4}
20	70			30			9.2×10^{-4}	1.6×10^{-4}
21	70	15		15			2.7×10^{-3}	4.2×10^{-4}
22[a]	70	20		10		46	8.2×10^{-3}	8.8×10^{-4}
23	40	45		15			2.4×10^{-3}	3.5×10^{-4}
24	30	67		3			3.1×10^{-3}	2.8×10^{-4}
25	15.5	81		3.5			2.2×10^{-3}	1.5×10^{-5}
26[b]		81	15.5	3.5		198	1.1×10^{-3}	9.5×10^{-5}
27[c]		81	15.5	3.5		225	1.2×10^{-3}	8.8×10^{-5}
28[c]		82	15		3	200	8.3×10^{-4}	9.2×10^{-5}

[a] The optimum preparation.

[b] Sulfided commercial catalyst.

[c] Nonsulfided commercial catalyst.

moters. Sample 11 is the AHM sample with no sulfiding, so it is molybdenum trioxide with some dioxide impurity. Sample 12 was sulfided. In both cases 30% molybdenum was deposited on the sample for a direct comparison with the 30% in sample 6. Other concentrations of molybdenum deposited by precipitation from ammonium heptamolybdate (samples 13 and 14) showed lower activities than samples 11 and 12.

Samples 26–28 are commercial catalysts, obtained from Harshaw Corp., in which molybdenum is deposited on alumina and a promoter, either nickel or cobalt, is added. These samples are not designed for methanation but they represent nonetheless a reasonably optimized dispersion of molybdenum on alumina with the added promoter. In these cases the concentrations of molybdenum and nickel are as follows: Sample 26 and 27 are Al_2O_3 supported with 3.5% Ni and 15.5% MoO_3. but sample 28 is Al_2O_3 supported with 3% cobalt and 15% MoO_2. Samples 1 and 16–18 are "blank" samples, with sample 1 the as-received MoS_2 powder; 16, molybdenum black; and 17 and 18 Ni supported on Al_2O_3. In samples 19–25 the Ni promoter was introduced as an inclusion on exfoliated MoS_2. Because nickel is itself an active catalyst for methanation it is not a priori clear in these cases why the use of the exfoliated molybdenum disulfide improves the activity. The exfoliated MoS_2 could offer a better dispersion of the nickel or the Ni/MoS_2 combination and could provide extra catalytic sites. In any case, these samples can be compared to the commercial samples 26–28.

Sample 19 is exfoliated MoS_2 in the presence of nickel only. As explained above in the discussion of inclusion compounds, the Ni does become attached to the MoS_2, and in this case it was determined afterward that the nickel was present to the concentration of 3%. This can be compared in turn to sample 17, where 3% Ni was supported on Al_2O_3. In sample 24 exfoliation was done in the presence of 67% $Al(NO_3)_3$ in order to improve the aluminum oxide/MoS_2 interaction. However, in this case the pH was not controlled so that the final pH was 11.3.

Sample 22 represents a sample prepared after studying in more detail the flocculation of molybdenum disulfide in an alumina suspension. It was found that for both of

TABLE 4

Methanation Rate for Various Catalysts, Calcined at 500°C and H_2 Reduced at 550°C

Sample No.	Composition (wt%)				BET surface area (m^2/g)	Rate after 20 hr (mole/g-catalyst/hr)	
	Exfoliated MoS_2	Al_2O_3	MoO_3	Ni		400°C	300°C
2	100				0.9	6.6×10^{-4}	7.4×10^{-5}
4	70	30				3.8×10^{-3}	4.6×10^{-4}
6	30	70			73	4.7×10^{-3}	5.3×10^{-4}
17		97		3	41	6.8×10^{-3}	3.3×10^{-4}
19	97			3		2.3×10^{-2}	1.2×10^{-3}
22[a]	70	20		10	46	[b]	1.3×10^{-2}
25	15.5	81		3.5		4.4×10^{-3}	3.7×10^{-4}
26[c]		81	15.5	3.5	198	1.6×10^{-3}	1.1×10^{-3}

[a] The optimum preparation.

[b] High production rate, 65% CO conversion.

[c] Commercial catalyst, sulfided.

these combinations very slow flocculation occurred at pH 6.2. Following this analysis the sample was prepared by exfoliating the molybdenum disulfide in water, adjusting the pH to 6.2, and adding a pH 6.2 suspension of alumina in a solution of nickel nitrate. The objective here was to attempt to reach as closely as possible the "desired configuration" shown in Fig. 1.

In all cases the catalysts presented in Tables 1–3, after forming by exfoliation, were dried and outgassed under vacuum at 400°C for 2 hr and calcined at 500°C for 1 hr. Then both methanation and TPD studies were made. Table 4 presents data of some of the calcined samples after a further treatment, normally reduction in a flow of hydrogen at 550°C for 1 hr.

3.2. Catalytic Studies

The catalytic studies for methanation were made by passing a mixture of hydrogen and carbon monoxide (Matheson-UHP) over the catalysts' bed at a rate of 5 to 1 with no recirculation. The total flow at 1 atmosphere pressure was 30 ml/min. The temperature of the catalyst was monitored by a Chromel–Alumel thermocouple to an accuracy of ±1°C. Measurements of the concentrations of CH_4 and CO_2 produced and also the remaining CO were made with a Varian gas chromatograph, using a 13× molecular sieve in series with a Porapak-N column. The sample size was varied in accordance with the activity, from 150 mg for exfoliated samples to 6 g for as-received MoS_2 and some of the oxides. The data for all prepared and commercial samples were taken with an accuracy of about 15%, after being 20 hr on stream. The initial activities were higher by a factor of about 2 for exfoliated samples and by a factor of about 5 for Ni on Al_2O_3.

The methanation rates reported in the tables are based on the concentration of CH_4 after a single pass (no recirculation). For some cases the total CO conversion was high and up to 30% of the CO was consumed. Although this cannot accurately be considered a differential rate, it is a satisfactory approximation for comparing rates. For cases where the conversion found to be more than 30% at 400°C, the approximation for a differential rate was considered inaccurate and we only show and compare the rates at low enough temperature (300°C) that less than 30% conversion occurs.

Some of the calcined and reduced exfoliated samples showed much higher activities (Table 4) than the calcined-only forms (Ta-

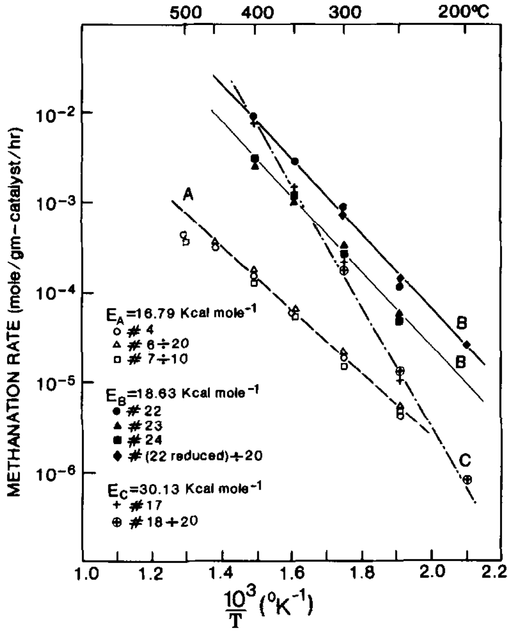


FIG. 2. Arrhenius plot of methanation rate vs temperature for various samples. A, exfoliated MoS_2 on Al_2O_3 with no promoter, with an activation energy of 16.79 kcal/mole; B, exfoliated MoS_2 with Ni as promoter atoms with an activation energy of 18.63 kcal/mole; C, Ni on Al_2O_3 with an activation energy of 30.13 kcal/mole. The methanation rates for some samples are normalized by factors of 10 and 20 for a more clear comparison.

ble 3). For example, the activity of sample 22 increased by a factor of 15 after reduction of its calcined form in H_2 at 550°C. But the blank Ni samples 17 and 18 did not show any higher activity upon reduction at the same temperature. Although these two samples showed very high activity at 400°C, activity dropped rapidly (*12*) when the temperature was lowered to 300°C, due to higher activation energies discussed in the next section. It was also observed that these samples poisoned easily within an hour or more with carbon monoxide on stream.

The aging of exfoliated samples was rather slow and could easily be recoverted to their original activities by re-reduction in hydrogen for an hour. This was simply done by cutting off the CO line and raising the temperature to 550°C, with H_2 gas on stream.

3.3. Activation Energies for Methanation

The activation energies of all samples are categorized into three groups. Group A, with an activation energy E_A = 16.79 kcal/mole, comprises the supported exfoliated samples with no promoters. Group C, consisting of blank Ni samples on support, showed an activation energy E_C = 30.13 kcal/mole. And finally group B, which covers almost all exfoliated samples with Ni promoters on Al_2O_3 support, has an activation energy E_B = 18.86 kcal/mole. Figure 2 shows the Arrhenius plot of the methanation rate versus the inverse temperature for these groups of samples. It should be noted that the methanation rate is "normalized" by dividing the activity by factors up to 20, as indicated in Fig. 2, in order that the three groups, A, B, and C, can be clearly identified.

3.4. Temperature Programmed Desorption

The methods of temperature programmed desorption were reported in an earlier contribution (*22*). Specifically, we have been interested in CO, O_2, and CO_2 adsorptions. The results are presented as the "effective area" for adsorption of each gas. We concluded that the coverage of CO_2 approximates the BET surface area of the MoS_2 samples (thus indicating the accessible MoS_2 basal plane of the sample). On the other hand, the effective area for CO and O_2 adsorption, which is lower, is believed to be associated with active sites on edge planes or edge atoms on single planes. Figure 3 shows a plot of the effective area for CO adsorption at room temperature versus methanation activity at 300°C. It is observed that there is a broad range of activity for various as-prepared samples. It is also observed that the activity seems to vary roughly as the square of the number of adsorption sites for CO. There seems to be less correlation between the density of CO_2 and O_2 adsorption sites and

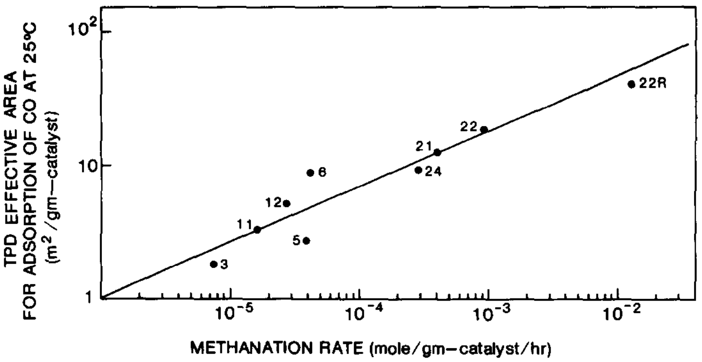


FIG. 3. Effective area of CO adsorption vs methanation activity at 300°C. The activity seems to vary roughly as the square root of the number of CO adsorption sites. Point at 22R represents sample 22 after reduction in H_2.

the catalytic activity. In case of CO_2 adsorption, the activity has an overall increase with increasing effective area, but the increase was more random rather than having a particular form.

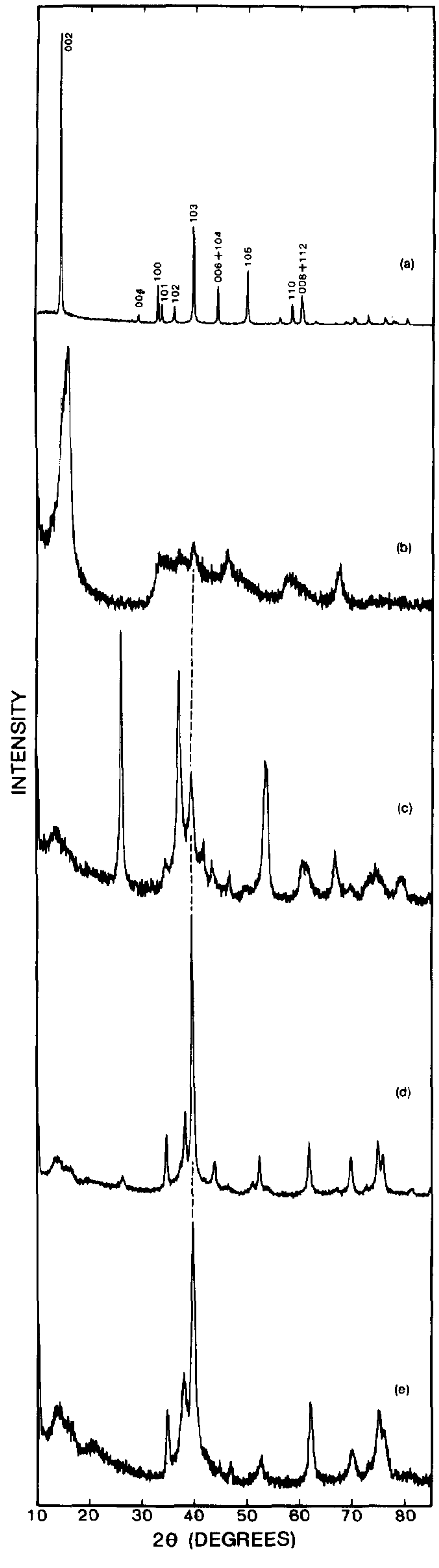
3.5. Auger Electron Analysis

Auger electron microscopy of samples showed a high level of carbon contamination on the surface. Consequently, the surface had to be sputtered with an Ar beam for 1 min, prior to the analysis, removing a layer of about 10–50 Å in depth. It was assumed that this sputtering removed any effects due to air exposure during transfer of the sample into the system. Both as-received and exfoliated samples with no support (samples 1 and 2) showed, as expected, an atomic ratio of S/Mo of 2 : 1, an indication for MoS_2 formulation. But the calcined samples, for example, sample 22, showed a molybdenum–oxysulfide composition of the form $MoS_{2-x}O_y$, with $x = 1$ and $y = 0.9$. No Ni line could be identified although Ni was present. When the calcined samples were reduced with H_2, the composition showed an oxysulfide of the form $MoS_{2-x}O_yNi_z$ with $x = 1.68$, $y = 0.62$, and $z = 0.43$. This indicated that the high activity sample 22 is mainly due to a Mo $S_{0.32}O_{0.62}Ni_{0.43}$ oxysulfide–nickel–alumina structure. A correlation of catalytic activity with the Mo/S ratio has been reported by others (*1, 29–31*). It should be pointed out that the oxygen content of these oxysulfides is higher by a factor of 2 to 4 prior to the surface sputtering. It seems that a preferential sputtering of oxygen may be the cause of the apparent low oxygen content measured in these samples.

3.6. X-ray Analysis of the Composition

The x-ray diffraction powder patterns of all samples were analyzed with a Philips diffractometer with an accuracy of ±0.1°, using Cu*Kα* radiation, with the following results:

(a) All exfoliated samples on alumina before calcination follow the normal pattern of monolayer MoS_2 with a strong (002) line at $2\theta = 14.4°$, similar to that of as-received MoS_2 presented in Fig. 4a. This is followed by a broad "monolayer" shoulder, decreasing toward the higher angles, on which relatively strong (100), (103), and (110) lines appear at 32.65, 39.60, and 54.35°, respectively. Superimposed on this pattern appear the three strongest lines of alumina at 37.25, 46.10, and 67.45°. Of course, going from sample 3 to sample 9 the MoS_2 pattern disappears and that of alumina appears more pronounced until sample 10, where it shows only the pattern of the pure alumina powder. This pattern is not shown in this set of figures; instead, a pattern for a Ni-promoted sample is presented in Fig. 4b.



This figure shows a broader (002) peak with a line shift, from 14.40 to 15.85°, an indication for a c-spacing contraction of about 9%. The FWHM of this peak is 2.05°, corresponding to a particle size of about 6 monolayers in thickness. The rest of the pattern is similar to that of a nonpromoted pattern, described earlier.

(b) Calcination of these samples makes three additional peaks appear on a distorted monolayer pattern. These peaks are located at 26.15, 37.10, and 53.75° and are attributed to a mixed phase of Mo oxides in the oxysulfide complex, described in the last section. See Fig. 4c.

(c) After subsequent reduction of the samples with hydrogen, the monolayer structure almost disappears and a new pattern with a very strong peak at 39.60° appears instead. We attribute this peak (see Fig. 4d) to an oxysulfide complex. It is noticed that the higher the catalytic activity, the sharper the 39.6° peak appears. It should be pointed out that although as-prepared samples of MoS_2 all have a peak at 39.6° due to the (103) line the oxysulfide peak at this angle is not due to MoS_2. Further investigation showed that the nonsupported exfoliated MoS_2, sample 2, also shows exactly the same pattern after calcination and reduction. See Fig. 4e. Thus it was concluded that this peak is due to oxysulfide structure only and is not due to either the Ni promoter or the alumina support. For further assurance, the results were compared with results on samples of NiO and NiS and also with published results (*32*, *33*) on various possible compounds. No equivalent line was found. An attempt was made to prepare an oxysulfide sample from MoO_3 and S with a sulfur deficiency at 500°C. The diffraction pattern of

FIG. 4. X-ray powder patterns (a) for untreated MoS_2, sample 1; (b–d) for exfoliated MoS_2 on Al_2O_3 with Ni promoter, sample 22 (b, as prepared; c, calcined at 500°C; d, calcined at 500°C and reduced in H_2 at 550°C); and (e) for the pattern for exfoliated MoS_2 with no support, sample 2, calcined and reduced at the same temperatures.

this sample also showed a peak at 39.6° but rather broad and less intense relative to those of oxysulfide from exfoliated MoS_2. The activity of this oxysulfide sample after calcination and reduction was of the same order of exfoliated MoS_2 with no support. See sample 2 of Table 4.

(d) The Ni lines from the blank Ni-supported alumina, samples 17 and 18, were dominated totally by the alumina pattern and thus no Ni lines were observed even for the case of sample 18, with 30% Ni on Al_2O_3. Samples 11–14 showed the normal Mo oxide pattern. Sample 15 indicated the lines due to a mixed phase of MoO_3 and MoO_2 rather than the expected MoO_2 only. The pattern was also quite different from that of the Mo metal, sample 16. The principal peaks due to Mo black appeared at 40.95, 68.75, and 78.95°. Samples 19–28 also followed the patterns described above, under (a), (b), and (c) groups accordingly.

3.7. Products and Product Ratios

In the case of catalysts based on exfoliated MoS_2, whether or not they contain a Ni promoter, the $CO_2 : CH_4$ ratio was found to be close to unity, with negligible water produced. On the other hand, the ratio for Ni supported on Al_2O_3 was very low with copious water generation. This is further support for the concept that the sites on exfoliated MoS_2/Ni are quite different from those on a Ni catalyst.

4. DISCUSSION

With the flocculation characteristics, suggesting a model for the catalyst as shown in Fig. 1, and the Auger and X-ray results, suggesting a break up of the layers of MoS_2 into an oxysulfide, a model for the active catalyst such as shown in Fig. 5 seems not inappropriate. In this figure a possible cross-sectional configuration is shown, in which the dispersed Ni atoms lie in between oxysulfide and alumina particles, keeping them further apart, and making more of the available active sites exposed for catalysis. The most important conclusion for the results, however, is that a catalyst of unusually high activity can be prepared using exfoliated MoS_2 with Ni as a promoter. In particular, we can compare the catalytic activity where the molybdenum is deposited by precipitation from ammonium heptamolybdate to that where it is prepared by exfoliation and then deposited onto the alumina support. With no promoter present we can compare the results on samples 11 and 12 (the AHM-based samples) to the results on samples 3 through 9 (the exfoliate-based samples). In samples 3 through 9 there seems to be a maximum activity at about 30% molybdenum disulfide. A similar maximum was obtained by depositing ammonium heptamolybdate which is why samples 11 and 12 were prepared with these concentrations. It is noted that the best sample prepared using exfoliated molybdenum disulfide is about 30 times more active than the best sample prepared by precipitation from ammonium heptamolybdate.

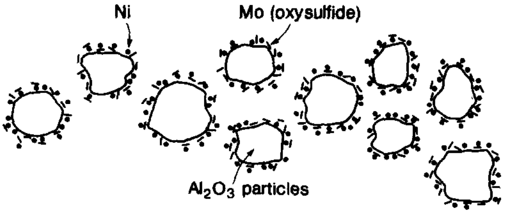


FIG. 5. The possible cross-sectional configuration of samples calcined at 500°C and reduced in H_2 at 550°C. The dispersed Ni atoms lie in between oxysulfide and Al_2O_3 particles, keeping them further apart and making more of the available active sites exposed for catalysis.

We can also compare promoted catalysts, specifically those promoted with nickel. With sample 18, where nickel was simply supported on Al_2O_3, the activity is high. At 400°C the activity of 3% Ni on Al_2O_3 (sample 17) is about the same as that of 10% Ni on exfoliated MoS_2/Al_2O_3 (sample 22 calcined). At 300°C, sample 22 has a higher activity than sample 17, although less than sample 18, with 30% Ni. But after reduction, which does not affect samples 17 and *18*, sample 22 at 300°C is a factor of 3 higher in activity than even sample 18. See Tables 2 and 3. We also can compare the activity of this group of samples to that of the commercial samples which include nickel (at 3.5%). We observe that the highest activity commercial catalysts are samples 26 and 27. It is observed that the activity of calcined and reduced sample 22 is on the order of 10 times higher than that of similarly treated sample 26 at 300°C.

We should also compare the methanation activity of our MoS_2 catalysts with methanation catalysts reported in the literature (*14*). The highest activity we are aware of is the order of 1.47×10^{-2} mole/g/hr at 350°C for a pure iron metal catalyst of 0.98 m^2/g surface area. The extrapolated result for reduced sample 22 at this temperature could be much higher than 6×10^{-2} mole/g/hr.

These results are suggestive that unusually high activity can, indeed, be obtained using exfoliated MoS_2 deposited on alumina with a promoter properly codeposited. This does not preclude the possibility that higher activities could be obtained (for example, using Raney nickel (*34*)), the important point here is the use of the MoS_2 which may render the catalyst more resistant to poisoning by sulfur (*13*).

The dependence of the activity on the active area for the carbon monoxide as measured by TPD is of some interest as well. The TPD effective area presumably relates to the density of sites for the adsorption of the various gases. In the plot of Fig. 3 the total areas under the TPD curves are represented by the ordinates, summing over all TPD peaks (*22*). The square root dependence of the activity on the CO site density may be of interest or it may be coincidence for the measurements we have made because samples 27–29, which have somewhat different origin than the other samples, do not follow the curve. If the relationship is valid, it is suggestive that adjacent sites that can aid CO adsorption are needed—it may, for example, be that adjacent sites for adsorption of CO and hydrogen are required for the methanation reaction.

In conclusion, the objective of this research was to deposit molybdenum disulfide in a single layer on alumina to form an incipient structure which can be converted into active sites such as recommended by Topsøe (*26–28*), while, at the same time, using the characteristics of MoS_2 flocculation to prevent multiple layers. To date our success in this direction has been only partial, but it does appear that catalysts prepared by recipes including exfoliated molybdenum disulfide may be designed with reasonable accuracy to provide unusually high activity catalysts—probably not only for methanation but also for hydrodesulfurization and hydrogenation catalysis.

ACKNOWLEDGMENTS

The authors acknowledge the support of this research by the National Sciences and Engineering Research Council of Canada. Acknowledgment is also du W. M. Sears and P. Joensen for valuable discussions, and to G. Scholz who was involved with preliminary studies (*35*).

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