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TPD and HYD Studies of Unpromoted and Co-Promoted Molybdenum Sulfide Catalyst ex Ammonium Tetrathiomolybdate

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Activity measurements of an unpromoted molybdenum sulfide catalyst prepared by the decomposition of ammonium tetrathiomolybdate (ATTM) indicate that the catalyst exhibits a higher HYD activity than a catalyst prepared by the conventional method of reductive sulfiding of the oxide, as well as a commercial catalyst. The increased activity can be attributed to a valence state of molybdenum lower than 4 in the supported sulfide catalyst and a concomitant increase in the number of anion vacancies as determined by TPD studies. The results also indicate that the addition of a promoter Co to ATTM results in higher HDS, but not higher HYD activity of the catalyst.

INTRODUCTION

Active sulfide catalysts are conventionally prepared by converting the respective oxides to sulfides. Reductive sulfiding of the oxides is usually difficult and does not proceed in a regular manner. On the other hand, a supported molybdenum sulfide catalyst can be prepared by the decomposition of ammonium tetrathiomolybdate (ATTM) in hydrogen or helium. The catalyst is unique in two respects, namely, the lower valence state of the supported molybdenum sulfide catalyst and the presence of few oxygen atoms in the catalyst (1). In the case of supported molybdenum sulfide, the lower valence state probably results in a higher concentration of anion vacancies (or coordinated unsaturation sites), which are believed to act as active sites of the catalyst. Therefore, it is quite likely that supported catalysts prepared by this technique will exhibit higher HDS and HYD activities compared to catalysts prepared by reductive sulfiding of the oxide. Such higher activities have been observed by the authors in the hydrogenolysis of thiophene and the results have been reported elsewhere (2).

In this article, the activity of a catalyst—prepared by the thermal decomposition of ATTM in helium followed by different pretreatments or hydrogen—in the hydrogenation of propylene are compared with the activities of both a conventional and a commercial catalyst. The pretreatment consists of flash or temperature-programmed decomposition of the supported ATTM in helium followed by removal of excess sulfur by temperature-programmed reduction (TPR) or by reduction in hydrogen. To understand the nature of the surface and catalytic sites, temperature-programmed desorption (TPD) of hydrogen sulfide has been conducted. The results from these studies and from HDS and HYD activity measurements of a cobalt-promoted molybdenum sulfide catalyst prepared by the decomposition of the thiosalt are also reported.

EXPERIMENTAL

Catalyst

Thermal decomposition of ATTM in helium produces molybdenum sulfide containing excess (nonstoichiometric) sulfur according to the reaction

$$(NH_4)_2MoS_4 \rightarrow 2NH_3 + H_2S + (3-y)S + MoS_y. \quad (1)$$

Two heating schedules for thermal decomposition were used: flash heating (done by lowering the reactor into a preheated oven) or temperature-programmed heating. In flash heating, the final temperature of 723 K was maintained for 1 h. In the case of temperature-programmed heating, the catalyst was heated at a rate of 10 K/min up to 723 K and held at that temperature for 15 min.

In some experiments, thermal decomposition of supported ATTM was carried out in a stream of H_2 instead of He. The heating rate was 15 K/min until the sample reached 823 K, and the sample was thereafter held at that temperature for 1 h. Thermal decomposition of supported ATTM in hydrogen produces molybdenum sulfide having a valence state lower than 4 (1) according to the reaction

$$(NH_4)_2MoS_4 + yH_2 \rightarrow (NH_4)_2S + yH_2S + MoS_{3-y}. \quad (2)$$

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The Co-promoted catalyst was prepared by impregnating vacuum-dried ATTM/Al_2O_3 with cobalt nitrate solution of appropriate concentration under a nitrogen blanket. The final catalyst (CTTM) had a dull gray color with a metal content equivalent to 3.0% CoO and 11.0% MoO_3. A commercial CoMo/Al_2O_3 catalyst (Harshaw 0402T, CoO 3%, MoO_3 15%), and conventional oxide catalysts, MoO_3/Al_2O_3 or Co–MoO_3/Al_2O_3, were used for comparison of catalyst activity. The conventional oxide catalyst was simply prepared by the calcination of ATTM/Al_2O_3 or CTTM/Al_2O_3 in a muffle furnace at 773 K for 12 h, and it therefore had the same Mo loading as the MoS_y catalyst.

Equipment

An integrated apparatus was used in this research, and a schematic of the apparatus is shown elsewhere (2). The system essentially consisted of a stainless-steel microreactor ($\frac{1}{4} \times 4\frac{1}{4}$ in.) equipped with a preheating coil and an arrangement of valves and tubing that permitted *in situ* preparation, pretreatment, pulse chemisorption, and activity measurement of the catalysts. A gas chromatograph (Hewlett–Packard 5890) was connected to the reactor through gas sampling valves to measure the temperature-programmed reduction/desorption profile and catalyst activity. The HP5890 chromatograph was interfaced to an IBM PC, and data acquisition and analysis were performed by a software, "Peak 96," supplied by Hewlett–Packard. All interconnecting tubings between the microreactor and the gas chromatograph were made of stainless steel. The lines connecting the injection port, the microreactor, and the line downstream of the reactor were wrapped with heating tape to prevent condensation of reactants. All the catalyst samples were prepared *in situ*. To reduce hold-up in the system, the intervening tubing was of narrow diameter ($\frac{1}{16}$ in.).

EXPERIMENTAL PROCEDURE

Pretreatment. Molybdenum sulfide catalyst prepared by the decomposition of ATTM or CTTM in helium was cooled to room temperature and subjected to one of the following pretreatments.

- Temperature-programmed reduction: The sample was heated at a heating rate of 15 K/min in hydrogen till it reached 823 K and then held at that temperature for 1 h. H_2S evolution was monitored by gas chromatography using an empty Teflon column of small diameter ($\frac{1}{4}$ in.).
- Reductive sulfiding: The catalyst was heated at 15 K/min in a 15.3% H_2S/H_2 mixture to 723 K and kept at that temperature for 1 h. After the sample was purged with He at 723 K for 15 min, it was cooled to room temperature and then subjected to TPR.

Temperature-programmed desorption (TPD). Molybdenum sulfide was prepared by thermal decomposition of ATTM/Al_2O_3 in He, after which the catalyst was cooled to room temperature and heated in H_2 at 15 K/min to 823 K until further sulfur loss was negligible. A 15% H_2S/H_2 mixture was passed through the pretreated catalyst (40 ml/min) at room temperature for 20 min to allow enough time for the H_2S to chemisorb on all accessible vacancies. After purging the catalyst with pure He at room temperature for 30 min to remove nonchemisorbed H_2S, the chemisorbed H_2S was desorbed by heating in hydrogen at 15 K/min to 823 K (TPD). H_2S evolution during TPD was determined from the total area under the TPD profile measured by gas chromatography and the H_2S calibration constant.

Measurement of catalyst activity. Propylene hydrogenation (HYD) was selected to test the hydrogenation activity of the catalysts. In propylene hydrogenation, the catalyst was cooled to 323 K after being subjected to different pretreatments as discussed earlier, and its activity was then determined by a continuous method. Propylene was mixed with H_2 at various concentrations by controlling the flow rate of each. The combined flow passed through the reactor at about 60 ml/min. Propylene and propane in the reaction product were analyzed by gas chromatography with a Durapak column at 303 K.

Thiophene hydrodesulfurization (HDS) was used as model reaction for measuring hydrogenolysis activity. The details of HDS activity measurement are described elsewhere (2).

RESULTS AND DISCUSSION

Propylene Hydrogenation

The fundamental premise in this article is that a lower valence state of Mo results in more anion vacancies (hence more coordinated unsaturation sites) probably leading to higher catalyst activities. Previous studies by Vasudevan and Weller (1) have shown that the catalyst prepared by H_2 reduction of ATTM on an alumina support has a valence state lower than 4, which is lower than the valence state of Mo(IV) in MoS_2–MoO_2 catalyst prepared by reductive sulfiding of conventional oxides. Results of activity measurements in the hydrogenolysis of thiophene (2) strongly support this hypothesis.

In a medium of hydrogen, MoS_2 is an *n*-type semiconductor, the excess electrons arising from the reaction

$$S^{2-} + H_2 \rightleftharpoons H_2S + \square_S + 2e^-,$$

where $\square_S$ is an anion vacancy (3). Due to the loss of sulfur anion, there is an excess of positive charge in the cation layer below, leading to the reduction of Mo^{4+} ions to lower oxidation states. It has been proposed that Mo^{3+} is the active site for HDS, implying a site containing two vacancies (4). Millman and Hall (5) have reported that two molecules of NO adsorb per site on reduced Mo/alumina, interpreting this as possible evidence for an Mo^{3+} site. Duben (6) has shown that adsorption of thiophene on a Mo^{3+} site can weaken the C–S bond and lead to a more pronounced HDS activity. There seems to be clear evidence from the literature that the average valence state of the reduced supported molybdenum sulfide catalyst is less than 4 (7–11). As far as HYD sites are concerned, Tanaka and Okuhara (12) have characterized them as coordinated unsaturation sites (CUS), that is, the number of anion vacancies per Mo site. According to their model, hydrogenation of olefins occurs on edge sites having three CUS.

It has been hypothesized that the creation of a large number of anion vacancies may lead to structural instability of the molybdenum sulfide crystallites and that in the presence of unsaturated molecules, these strong acidic sites may be deactivated faster (3). Consequently, even though the initial activity of a catalyst containing more anion vacancies may be higher, the long-term performance of such a catalyst could be poor due to its rapid deactivation. As mentioned earlier, in thiophene hydrogenolysis, the activity of a catalyst prepared by the decomposition of ATTM was found to be consistently superior to a catalyst prepared by reductive sulfiding of the oxide (and having the same Mo loading) (2), even at long times and at high conversions. Hence, in carrying out such experimental studies, it is important to assess the performance of the catalysts under conditions where the stability of the catalyst can be evaluated.

The determination of the nature of the hydrogenation reaction on molybdenum sulfide catalyst is also a subject of considerable interest. In the present study, propylene hydrogenation was selected as a model reaction due to its good conversion at low temperatures. Hydrogenation of olefins is very easily accomplished at low temperatures. Deactivation of the catalyst caused by preferential adsorption of unsaturated hydrocarbon (13) is a problem in acquiring data for activity comparison. The effect of temperature on propylene hydrogenation was investigated at reaction temperatures of 323, 373, and 423 K. A continuous method was used to monitor propylene conversion as a function of time. To minimize the deactivation rate, all the runs were conducted at 323 K.

The results of propylene hydrogenation activity measurements for the two pretreatments (flash and temperature-programmed decomposition) are shown in Fig. 1. The conversions for both pretreatments are very close, and the catalysts subjected to the two pretreatments appear to be fairly stable. For unsupported ATTM subjected to similar pretreatments, Kalthod and Weller (14) concluded that both basal and edge planes provide almost the same hydrogenation activity after temperature-programmed reduction. However, it is widely believed that hydrogenolysis and hydrogenation occur at edges and corners, and not at the basal plane (15). Single crystal studies by Tanaka *et al.* have shown the reactivity of the edge plane toward olefin hydrogenation, and according to them and other research groups, hydrogenation occurs where there are three coordinated unsaturation sites (12, 16). Daage and Chianelli (17) have recently shown that in the case of dibenzothiophene, hydrogenation occurs exclusively on the "rim" (or corner) sites, whereas hydrogenolysis can occur on both edge and corner sites. It therefore appears that the number of corner sites are about the same and therefore independent of the method of pretreatment (flash vs temperature-programmed decomposition), in the case of supported molybdenum sulfide catalysts prepared by the decomposition of ATTM. It is interesting to see from Fig. 1 that even after 180 min into the run, the conversions are lower, but essentially the same for the two pretreatments. Also, in thiophene HDS (2), the conversions (although much lower) were essentially found to be the same for the two pretreatments.

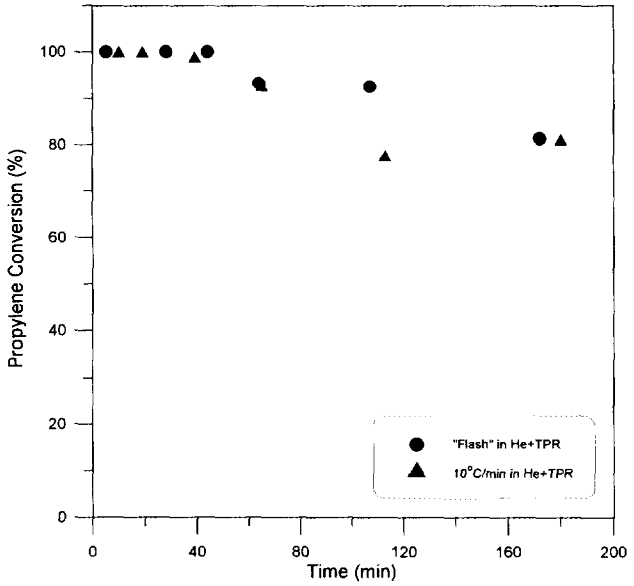

FIG. 1. Effect of the thermal decomposition heating rate on HYD activity. Catalyst weight, 0.2 g. *T*, 323 K. $H_2:C_3H_6$ = 1.5:1. Catalysts prepared by flash and 10 K/min thermal decomposition of ATTM in He followed by TPR.

The effect of catalyst preparation technique on propylene conversion is shown in Fig. 2. For reactant concentration at $H_2:C_3H_6 = 1.5:1$, the MoS_y/Al_2O_3 catalyst prepared by hydrogen reduction of ATTM showed the highest propylene HYD conversion; the Harshaw 0402T catalyst prepared by reductive sulfiding had an intermediate conversion and the conventional oxide catalyst with the same Mo loading as the MoS_y/Al_2O_3 catalyst, and prepared by

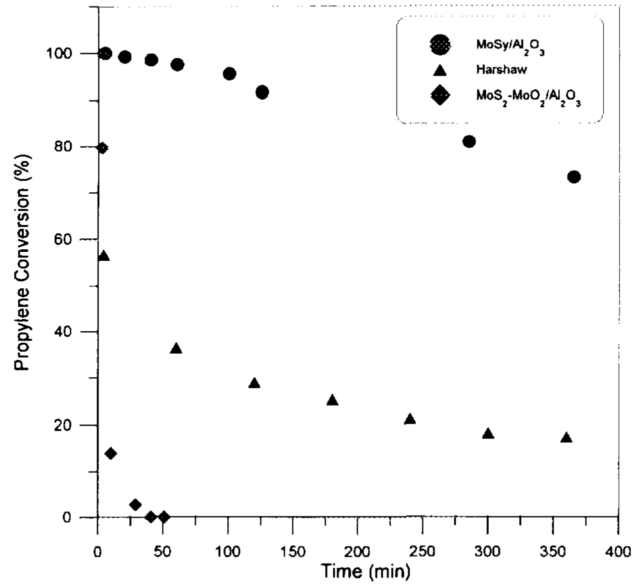

FIG. 2. Effect of catalyst preparation on HYD activity. Catalyst weight, 0.2 g. *T*, 323 K. $H_2:C_3H_6 = 1.5:1$. MoS_y/Al_2O_3 prepared by the reduction of ATTM in H_2. MoO_2–MoS_2/Al_2O_3 and Harshaw 0402T prepared by reductive sulfiding followed by TPR.

reductive sulfiding, was the least active. Comparison with the commercial Harshaw catalyst may appear to be unjustified, but it is interesting to note that unlike the ATTM/Al_2O_3 catalyst, the Harshaw catalyst had a much higher Mo loading (MoO_3 15% vs MoO_3 11%) and was also promoted with cobalt (CoO 3%). In spite of this, the Harshaw catalyst showed a lower activity. The reaction rates in the above case for the ATTM/Al_2O_3, Harshaw, and the conventional catalyst were 4.8×10^{-4}, 2.8×10^{-4}, and 3.8×10^{-4} mmol/m$^2 \cdot$s, respectively. However, it is clear from Fig. 2 that the reaction rate for the conventional catalyst drops rapidly, and the rate is 6.8×10^{-5} mmol/m$^2 \cdot$s after 10 min. Clearly, the MoS_y/Al_2O_3 catalyst prepared by hydrogen reduction of ATTM is superior.

The catalyst prepared by H_2 reduction of ATTM/Al_2O_3 showed a much higher HYD activity than the conventional oxide catalyst probably due to the following reasons. During reductive sulfiding, conventional oxide catalysts are not completely converted into sulfides (13, 18). XPS results have also indicated that the sulfiding is incomplete (19). Since the sulfur atom is a greater electron donor than an oxygen atom, this results in an increase in the electron density of the molybdenum ions on the surface of the catalysts created during reduction. The higher electron density probably leads to an enhanced electron donation to the reactant molecule, thus increasing the activity per site of the catalyst.

It is clear from the plots of propylene conversion versus time that deactivation is prevalent in all the catalysts under the reaction conditions specified above. As mentioned earlier, the deactivation of catalyst during olefin hydrogenation is usually caused by preferential adsorption of unsaturated hydrocarbon (13). It is interesting to note that even though deactivation is observed with time, the activity of the hydrogen-reduced catalyst is consistently higher than the activities of the Harshaw or conventional oxide catalyst, and thus it appears to have a fairly good structural stability. It is also clear from the plot that if the reactor had been operated in a manner in which the conversions were low, it would have been extremely difficult to assess the performance of the conventional catalyst prepared by reductive sulfiding of the oxide since the conversion would have probably been close to zero (see Fig. 2). In any case, the conventional catalyst was prepared by calcining the ATTM/Al_2O_3 precursor followed by reductive sulfiding so as to ensure that it had the same Mo loading. Hence from both measurements of reaction rate (based on surface area) and long-term performance, the hydrogen-reduced ATTM/Al_2O_3 catalyst appears to be superior, even though it is unpromoted.

The propylene conversion versus time at different initial propylene concentrations is shown in Fig. 3. It can be observed that when the ratio of hydrogen to propylene in the initial reactant is increased from 1.5 : 1 to 3 : 1, the extent of deactivation decreases. This suggests that deactivation is more rapid when the partial pressure of propylene in the initial reactant is higher.

Regeneration of the catalyst by conducting a temperature-programmed reduction in hydrogen at 15 K/min to

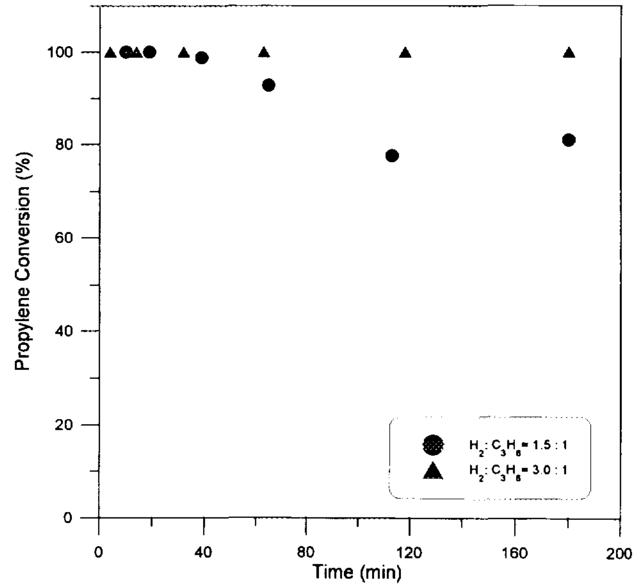

FIG. 3. Effect of reactant concentration on HYD activity. Catalyst weight, 0.2 g. *T*, 323 K. Catalysts prepared by 10 K/min thermal decomposition of ATTM in He followed by TPR.

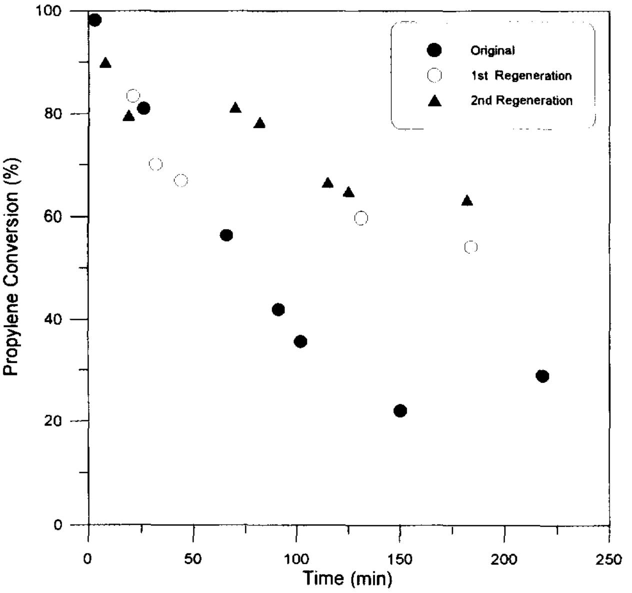

FIG. 4. Catalyst regeneration by heating in H_2 at 15 K/min to 823 K. Catalyst weight, 0.08 g. T, 323 K. $H_2:C_3H_6$ = 1.5:1. Catalysts prepared by 10 K/min thermal decomposition of ATTM in He followed by TPR.

823 K was investigated. It was found that the original catalytic activity could be regenerated after heating. Furthermore, the regenerated catalysts exhibited a much lower deactivation rate compared to fresh catalyst probably due to a better dispersion of the catalyst. The propylene conversions versus time for a fresh catalyst and for the same catalyst after the first and second regeneration are shown in Fig. 4. Note that deactivation is more pronounced in this case since the catalyst weight is 0.08 g compared to Figs. 2 and 3, in which the catalyst weight is 0.2 g. Since deactivation is mostly caused by adsorption of propylene, heating in hydrogen can remove the propylene from active sites and therefore recover catalytic activity. Ethylene hydrogenation conducted on MoS_2–WS_2/Al_2O_3–SiO_2 catalysts to study the deactivation effect of adsorbed ethylene has proved that the deactivation takes place only after the saturation of active catalyst surface with ethylene (13).

Temperature-Programmed Desorption

Generally, the coordinated unsaturation sites and associated anion vacancies are considered to be the active sites for HDS and HYD reactions. An approach to studying the anion vacancies is to measure the H_2S evolution from the surface during temperature-programmed desorption of H_2S. The TPD measurement method was described in the experimental section. The H_2S evolution during TPD represents the amount of surface anion vacancies of a catalyst. The results of TPD experiments are listed in Table 1. LTOC and HDS activity data are cited from a previous paper from this group (2).

After thermal decomposition of ATTM/Al_2O_3 in He at 10 K/min to 723 K, the catalyst was subjected to TPR to 693 K (or 823 K) followed by TPD to the same temperature. The temperature just beyond the first TPR peak is 693 K. The H_2S TPD peaks for different reduction temperatures are shown in Fig. 5. Not surprisingly, it can be seen that when the sulfur was further removed by conducting TPR to 823 K, there was a big increase in the peak area under TPD curve (b), compared to the peak area under curve (a). Since the peak area corresponds to the removal of H_2S from the surface, the catalyst in which TPR was conducted to 823 K had more surface anion vacancies. The LTOC value and thiophene activity were also higher after the second TPR peak, which corresponds to an increase in anion vacancies in the edge plane.

The H_2S evolution for a flash-decomposed sample is 19.0 ml/g, which is higher than 15.0 ml/g for a 10 K/min decomposed sample. This suggests that more surface anion vacancies are formed for flash-decomposed samples compared to 10 K/min decomposed samples. Since the LTOC value and HDS/HYD activity of the catalyst for flash-decomposed samples are nearly the same as that for the 10 K/min samples, it is possible that the flash-decomposed samples have a smaller edge area, or a smaller number of corner sites than the 10 K/min decomposed sample.

If oxygen chemisorbs dissociatively with one atom on each anion vacancy, the ratio of H_2S evolved/LTOC should equal to 2. However, this ratio is much higher than 2 for

TABLE 1

Temperature-Programmed Desorption of H_2S

Catalyst	Pretreatment	TPD H_2S (ml/g)	LTOC (ml/g)	HDS activity conversion (%)
ATTM/Al_2O_3	Flash + TPR	19.0	1.31	68.0
ATTM/Al_2O_3	10 K/min + TPR (823 K)	15.0	1.42	70.4
ATTM/Al_2O_3	H_2 reduction	19.0	0.79	71.3
ATTM/Al_2O_3	10 K/min + TPR (693 K)	10.1	0.66	56.0
MoO_3/Al_2O_3	H_2S/H_2 + TPR	10.7	0.55	55.0
Harshaw 0402T	H_2S/H_2 + TPR	7.26	0.19	66.5

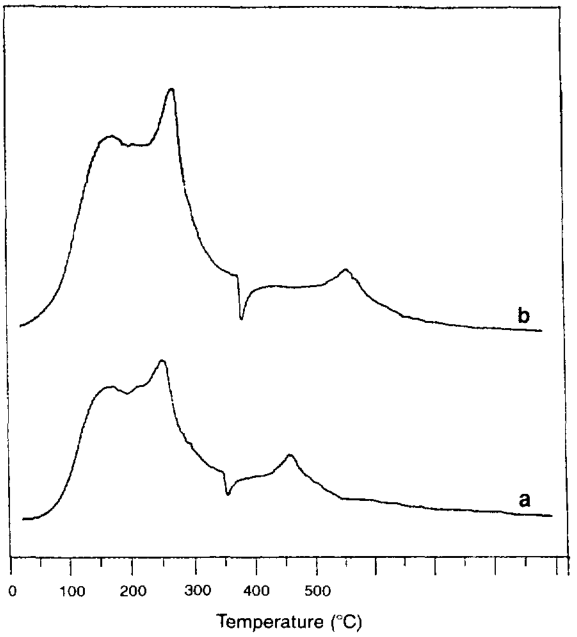

FIG. 5. Effect of reduction temperature on TPD profiles. Catalyst weight, 0.2 g. Catalysts prepared by thermal decomposition of ATTM at 10 K/min in He followed by TPR to (a) 693 K; (b) 823 K.

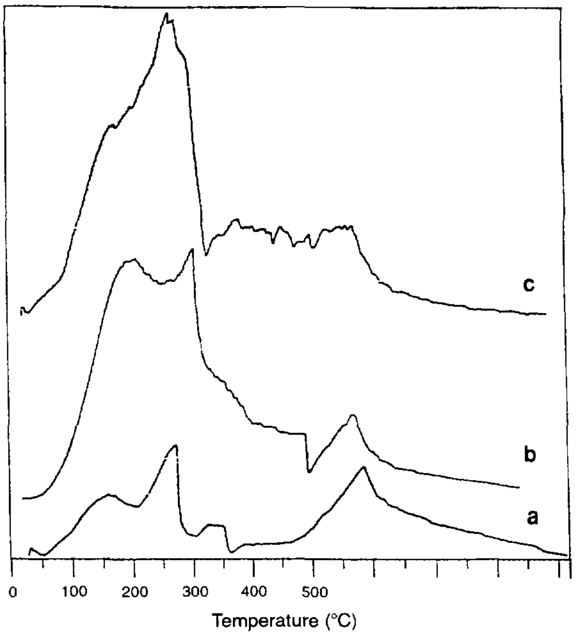

FIG. 6. Effect of preparation technique on TPD profile. Catalyst weight, 0.2 g. (a) Harshaw 0402T: Reductive sulfiding + TPR. (b) MoO_3/Al_2O_3: Reductive sulfiding + TPR. (c) $ATTM/Al_2O_3$: H_2 reduction.

the catalysts in our study. This suggests that a particular geometrical configuration of vacancies, such as a pair of adjacent vacancies, is necessary to adsorb oxygen. The same interpretation has been suggested by Millman and Hall (20) for MoO_2/Al_2O_3 catalysts and has been observed by Kalthod and Weller for unsupported ATTM (14).

Comparison of the TPD profile for catalysts with different preparation techniques is shown in Fig. 6. The MoS_y/Al_2O_3 catalyst prepared by decomposition of ATTM in hydrogen showed the highest H_2S evolution. The conventional oxide catalyst with the same Mo loading as the MoS_y/Al_2O_3, prepared by reductive sulfiding had an intermediate H_2S evolution. The Harshaw 0402T had the least amount of H_2S evolution. This suggests that of the three, the catalyst prepared by hydrogen reduction had the highest amount of surface anion vacancies and possibly more edge/corner sites. This is supported by the activity measurements for thiophene HDS and propylene HYD reactions. The conventional oxide catalyst had more anion vacancies than Harshaw 0402T according to TPD and LTOC measurements. But it had a lower activity for HDS and HYD than the Harshaw catalyst. However, it is important to remember that unlike the conventional oxide catalyst, the Harshaw catalyst is promoted with cobalt.

Cobalt-Promoted Molybdenum Catalyst

The effect of adding a Co promoter on Mo/Al_2O_3 prepared by the impregnation of $ATTM/Al_2O_3$ with cobalt nitrate solution was investigated through measurements of oxygen chemisorption and HDS and HYD activity. LTOC, BET values, and propylene HYD and thiophene HDS conversions for promoted and unpromoted catalysts are shown in Table 2. The unpromoted $ATTM/Al_2O_3$ shown in Table 2 was subjected to a similar pretreatment (thermal decomposition in He followed by TPR). The experiments wre repeated to ensure reproducibility of data.

It can be seen that the BET surface area of molybdenum catalyst decreases due to the addition of a promoter. The oxygen chemisorption of promoted molybdenum catalyst was higher compared to that of the unpromoted catalyst. The propylene HYD conversion during a 5-h reaction period and the thiophene HDS conversion during a 3.5-h reaction period are shown in Figs. 7 and 8, respectively. It can be observed that for the Co-promoted catalyst, the HDS activity increased significantly, but the HYD activity

TABLE 2

Comparison of Co-Promoted and Unpromoted $ATTM/Al_2O_3$

Catalyst	LTOC (ml/g)	BET area (m^2/g)	TPD (ml/g)	HYD conv. (At t = 3 h, %)	HDS conv. (ave %)
$CTTM/Al_2O_3$	2.31	155	15.4	30.3	54.1
$ATTM/Al_2O_3$	1.42	183	15.0	28.9	13.5

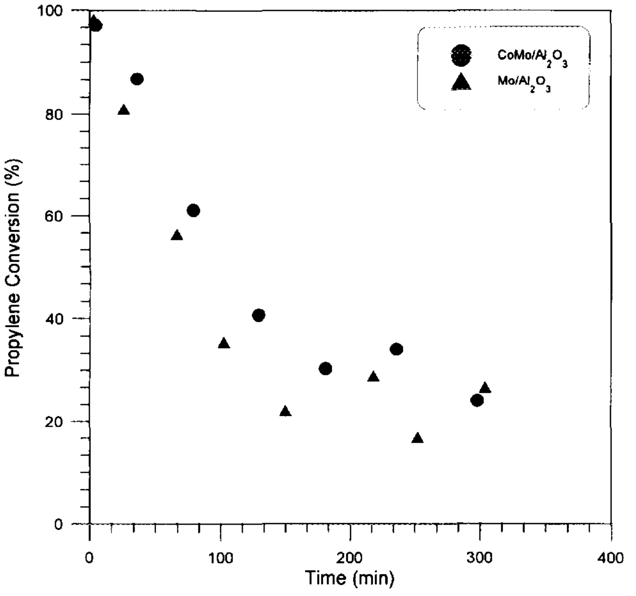

FIG. 7. Propylene HYD activity for Co-promoted and unpromoted catalysts. Catalyst weight, 0.08 g. T, 323 K. $H_2:C_3H_6 = 1.5:1$. Catalysts prepared by thermal decomposition of CTTM and ATTM in He at 10 K/min followed by TPR.

was very similar to that of the unpromoted catalyst (conversions were almost the same at all times). It has been proposed (21, 22) that for HDS reactions, Co as a promoter changes the intrinsic activity of the HDS sites by altering the electron density around Mo. The promoted catalysts have a higher HDS activity per site (CUS) than the unpromoted catalyst. But unlike the HDS sites, Reddy *et al.* believe that the promoter does not alter the intrinsic activity of the HYD sites (22). Therefore, the HYD reaction appears to be a function of the number of active sites only, which is in agreement with our observation. Also, since the HYD activity of Co-promoted catalyst is not higher than the corresponding activity for the unpromoted catalyst, it appears that LTOC does not correlate well with HYD activity for the Co-promoted catalyst. Prins *et al.* (23) have argued that although oxygen chemisorption is useful for ranking catalysts, it is a corrosive method, and hence not useful for a fundamental understanding of the catalyst surface.

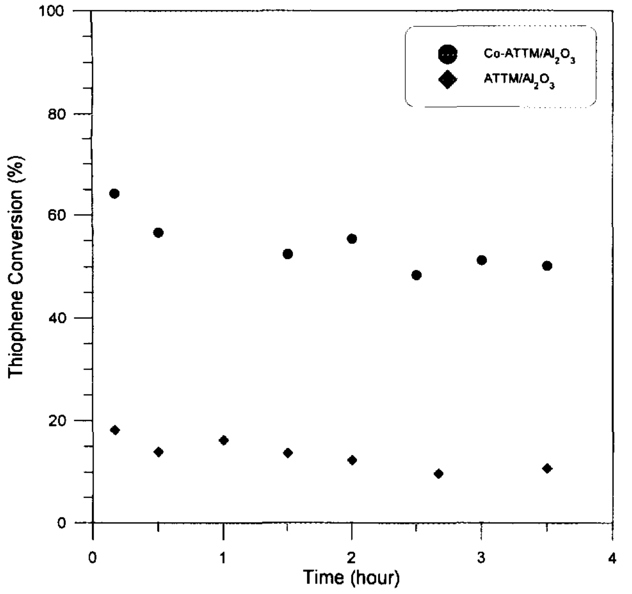

FIG. 8. Thiophene HDS activity for Co-promoted and unpromoted catalysts. Catalyst weight, 0.2 g. Catalysts prepared by thermal decomposition of CTTM and ATTM in He at 10 K/min followed by TPR.

The H_2S evolution during TPD for supported Co-promoted and unpromoted ATTM is reported in Table 2. It is clear that the H_2S evolution of the Co-promoted catalyst is almost the same as that of the unpromoted catalyst. This suggests that cobalt promotion does not increase the anion vacancies in the surface. Different arguments have been presented about the role of cobalt as a promoter in HDS catalysts. The role of cobalt is still not very well understood even through the location of the promoter is well known. Mossbauer studies conducted by Wivel *et al.* (24) established that the promoter effect of cobalt is related to the cobalt ions adsorbed on MoS_2. The promoter effect does not appear to be due to separate Co_9S_8 crystallites but due to cobalt ions in contact with the catalyst. Topsoe and Topsoe claim that the cobalt ions are located at the edges of the molybdenum plane of a MoS_2 layer, thus extending the layer (Co–Mo–S phase) (21). Harris and Chianelli (25) have proposed that the electron density at the Mo sites is increased by Co or Ni promoter ions and that the modified, reduced Mo sites have a higher activity. While some researchers claim that cobalt increases the number of active sites (26), others favor the idea that cobalt does not affect the number of active sites but promotes the intrinsic activity of the sites (27–29). Based on our observation of TPD and HDS/HYD activities, it appears that cobalt affects the intrinsic activity (increases HDS, not HYD activity) rather than the number of active sites.

The effect of preparation technique on Co-promoted catalysts is shown in Fig. 9. Propylene HYD activities of the two catalysts prepared from Co-promoted ATTM/Al_2O_3 and Co-promoted MoO_3/Al_2O_3 are compared. It can be observed that for the same catalyst weight and pretreatment, the Co-promoted ATTM/Al_2O_3 had a much higher activity than the conventional oxide catalyst (reaction rates were 13.9×10^{-4} and 6.3×10^{-4} mmol/m$^2 \cdot$s, respectively). Deactivation is more pronounced in Figs. 7 and 9 because the weight of the catalyst is only 0.08 g, unlike Figs. 2 and 3 for the unpromoted catalyst in which the catalyst weight is 0.2 g. The extent of reduction of the Co-promoted ATTM/Al_2O_3 has not been reported in the literature. But judging by the results for the catalyst pre-

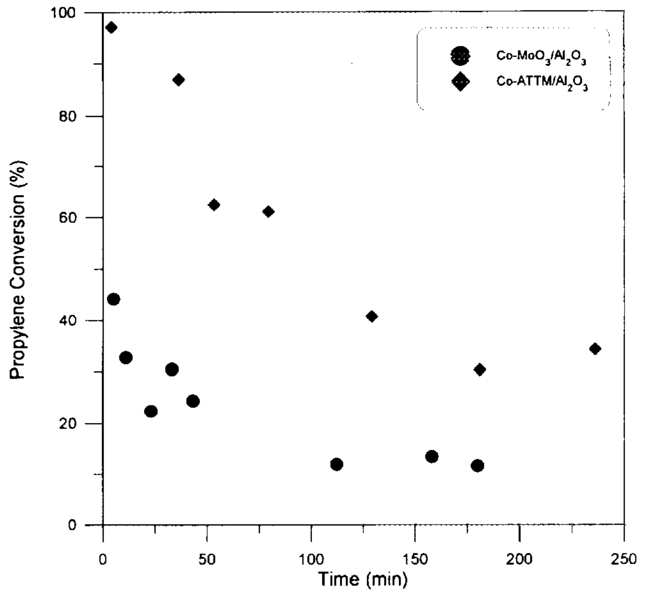

FIG. 9. Propylene HYD activity for Co-promoted ATTM/Al_2O_3 and Co-promoted MoO_3/Al_2O_3. Catatlyst weight, 0.08 g. *T*, 323 K. $H_2:C_3H_6$ = 1.5:1. Catalysts prepared by (a) thermal decomposition of CTTM in He at 10 K/min followed by TPR. (b) Co–MoO_3/Al_2O_3 prepared by reductive sulfiding followed by TPR.

pared by the decomposition of ATTM in hydrogen, one can surmise that the valence state of molybdenum prepared from Co-promoted ATTM/Al_2O_3 is probably lower than the valence state of a Co-promoted conventional oxide, resulting in more surface anion vacancies, thus leading to the higher activity. The experimental results support this assumption. However, as mentioned earlier, the role of Co is still not clear. Duchet *et al.* (30) have suggested that cobalt sulfide may act as the catalyst instead of the promoter. It is well known that sulfided cobalt on alumina has a low HDS activity due to its strong interaction with alumina during catalyst preparation. A higher activity for CoMo is obtained when in the preparation procedure, the Mo is impregnated first. However, this model does not explain the difference in activities between the conventional reductively sulfided promoted catalyst and the promoted catalyst prepared by the decomposition of ATTM in hydrogen. It is clear that in addition to the role of cobalt, the number of anion vacancies (CUS) also plays a key role in the activity of the catalyst.

SUMMARY AND CONCLUSIONS

The effect of various pretreatments on HYD activity of supported molybdenum sulfide catalyst prepared by the decomposition of ATTM/CTTM has been investigated. The pretreatment consisted of flash or temperature-programmed decomposition of the supported ATTM/CTTM in helium followed by removal of excess sulfur by temperature-programmed reduction or the decomposition in hydrogen. The catalyst prepared by thermal decomposition of supported ATTM had a much higher HYD/HDS activity than the conventional oxide catalyst or a commercial catalyst. The catalyst activity appears to have a direct correlation with the valence state of Mo, and consequently with the number of anion vacancies (CUS).

H_2S evolution during TPD and the activity of the catalyst increased with H_2 reduction temperature. This may be attributed to the nonstoichiometric sulfur atoms blocking CUS-Mo sites at the crystallite edges at lower temperatures. The heating rate during thermal decomposition had little effect on HYD activity.

Cobalt promotion increased thiophene HDS activity significantly, but it did not increase HYD activity. TPD results showed that Co promotion increased the intrinsic activity rather than the number of active sites.

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