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Studies of Molybdenum Sulfide Catalysts: Effects of Pretreatment on Olefin Hydrogenation Activity

INTRODUCTION

Various models have been proposed for the active sites in hydrogenation and hydrogenolysis reactions on molybdenum sulfide catalysts (*1–19*). The role played by edge and basal sites of the sulfide in both oxygen chemisorption and in hydrogenation is still moot, although the question has been often investigated (*8–10, 13–18*). We have chosen to study the effect of catalyst preparation and pretreatment on the properties of unsupported molybdenum disulfide, to avoid some of the problems involved in characterizing supported catalysts. The unsupported sulfide was prepared *in situ* by the thermal decomposition of ammonium tetrathiomolybdate (ATTM) in flowing helium.

As reported in a previous paper (*35*), ATTM decomposition leads to a poorly crystalline, nonstoichiometric sulfide with an atom ratio S/Mo = 2.3–2.4. There are indications that the morphology of the sulfide may depend on details of the ATTM decomposition (sample size, heating rate). When the sulfide is heated in hydrogen, the excess sulfur is evolved as hydrogen sulfide, and the TPR spectrum shows two peaks centered at about 180 and 380°C. Sintering is negligible during the first peak (i.e., when the TPR is stopped at 250°C); sintering occurs during traverse of the 250–450°C TPR range and increases with increased holding time at 450°C. The sample stoichiometry is S/Mo = 2.0 after TPR to 450°C. As sulfur is removed, the low-temperature oxygen chemisorption (LTOC) increases dramatically, and the ratio of total (BET) surface area to oxygen chemisorbed decreases to the range 70–80 Å^2/O$_2$ after reduction to 450°C.

In the present paper, unsupported molybdenum sulfide catalysts prepared by ATTM decomposition have been tested for catalytic activity in propene hydrogenation after various pretreatments. This was selected as a test reaction because it gives good conversions at temperatures below the TPR peaks; these mild conditions do not destroy the effects of catalyst pretreatment. Activity was measured with a pulse method, with determination of kinetic constants by a procedure recently described (*37*).

EXPERIMENTAL

Apparatus

An integrated microreactor system (*35*) was used, in which it was possible to measure temperature-programmed reduction (TPR) spectra, reaction rates, oxygen chemisorption, and BET area on a catalyst sample prepared *in situ* and subjected to a desired pretreatment.

Catalysts

Ammonium tetrathiomolybdate (ATTM), prepared in crystalline form as described in (*36*), was decomposed by heating in flowing He to yield molybdenum sulfide. The ATTM was supported between glass wool plugs and decomposed in the microreactor; there was no exposure of the resulting sulfide to air in any of the subsequent tests. Usually 0.3 g of ATTM was used in these experiments. The ATTM was decomposed

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by "flash heating", done by lowering the reactor into a preheated furnace; the time to reach 450°C was about 6 min. Small sample size and flash heating has been previously shown to lead to molybdenum sulfide of relatively high surface area and high oxygen chemisorption (*35*).

Pretreatment

After decomposition of ATTM in He, the product sulfide was cooled to room temperature and subjected to one of the following pretreatments:

(a) Temperature-programmed reduction (TPR): The catalyst was heated at a constant rate in flowing hydrogen. Evolution of hydrogen sulfide was monitored by passing the reactor effluent in the thermal conductivity detector of a gas chromatograph (GC). The final TPR temperature was typically 450°C.

(b) Reductive sulfiding: The catalyst was heated at 15°C/min in 15% H_2S/H_2 to 450°C for 60 min. After the sample was purged with He at 450°C, it was cooled in He to room temperature and then subjected to TPR as in (a).

Activity Measurement

After pretreatment, the catalyst was cooled to 100°C and its activity for propene hydrogenation determined by a pulse method. Rate parameters were deduced by a method recently described (*37*); the method depends on variation of conversion with pulse volume. Analysis of propene and propane in the effluent was by GC (Hewlett-Packard 5754), with a $\frac{1}{4}$ in. × 6 ft column of Durapak (*n*-octane on Porasil-C) operating at room temperature. A slight initial deactivation was followed by a steady level of conversion, after five to eight injections of propene, at the test temperatures of 100 and 150°C. The apparent energy of activation was calculated from the difference in rate constant at these two temperatures. The specific rate constants listed in the tables are corrected for catalyst (BET) surface area; units are mols propene converted per unit time per unit surface area.

Oxygen Chemisorption and BET Area

Low-temperature oxygen chemisorption (LTOC) at −78°C was determined by a pulse method. Pulse of 1.5% O_2/He were injected in the He carrier gas (25 cm^3/min) which passes through the catalyst bed and into the GC for measurement of unadsorbed O_2. The catalyst was considered saturated when three successive peaks of equal area emerged.

An Isorpta analyzer was used to determine the BET area by N_2 adsorption at −195°C. The N_2 partial pressure was changed by progressive increases in total pressure of a 7% N_2/He stream flowing continuously over the catalyst.

Hydrogen Sulfide Evolution and S/Mo Ratios

The H_2S evolved during TPR was absorbed in zinc acetate solution and measured by iodometric titration. The cumulative H_2S evolution was also determined from the total area under the signal from the GC and the H_2S calibration constant. The two values agreed within 10–15% in all cases. The S/Mo ratio for the initial catalyst before TPR was determined from the weight loss in oxidizing the sulfide to MoO_3 in a muffle furnace at 550°C for 60 min, a standard analytical method for Mo. If only S and Mo are present, the estimated maximum error in the S/Mo ratio is about 0.04. The S/Mo ratios of the catalysts after heating in hydrogen were calculated from the S/Mo ratio for the initial catalyst and the H_2S evolution during TPR.

RESULTS

Effect of TPR Temperature and Time

It was shown previously (*35*) that molybdenum sulfide prepared by decomposition of ATTM exhibits a TPR spectrum with peaks at around 180 and 380°C. In view of this, we thought it desirable to study cata-

TABLE 1

Effects of TPR Temperature and Time on Catalyst Properties

Run No.	Final T^a (°C)	Time at final T (min)	S/Mo	k_s (150°C) (mol × 10^{10} cm^{-2} s^{-1})	E_{app} (kcal mol^{-1})	S(BET) (m^2 g^{-1})	LTOC (cm^3 (STP) g^{-1})	k_s/O_2 (mol mol^{-1} s^{-1})
1	250	0^b	2.32	0.014	7.4	39.8	0.44	0.028
2	450	0^b	2.12	0.71	3.7	13.9	0.63	0.35
3	450	60	2.05	1.4	2.8	9.0	0.27	1.0

[a] Sample was subjected to TPR (15°C/min) to the final temperature indicated.

[b] Sample was purged with He as soon as the indicated final temperature was reached.

lytic behavior at different points on the TPR curve. The "cut points" chosen for investigation were (a) 250°C (corresponding to a trough between the two TPR peaks), followed by immediate He purge and cooling; (b) 450°C (corresponding to completion of the second TPR peak), followed by immediate He purge and cooling; and (c) 450°C, with hydrogen flow for 1 hr at 450°C before He purge and cooling. The results are summarized in Table 1. Shown in the table are the stoichiometry (S/Mo ratio); specific rate constant at 150°C for propene hydrogenation, k_s; apparent activation energy deduced from the rate constants at 100 and 150°C; total (BET) area; oxygen chemisorption at −78°C (LTOC); and the ratio of specific rate constant to oxygen chemisorbed, which may be considered as a kind of turnover number.

Prior to the pretreatments shown in Table 1, the molybdenum sulfide had a S/Mo ratio of 2.40 and surface area of 36 m^2/g; it showed very little oxygen chemisorption and had almost no hydrogenation activity at 150°C. By the time the TPR had been carried to 250°C (Run 1), substantial capability for oxygen chemisorption developed but the hydrogenation activity was still very small; sintering was negligible at this point. TPR past the second peak (Run 2) resulted in incremental S removal, severe sintering, a further increase in LTOC, and a 50-fold increase in specific rate constant for hydrogenation. The activation energy for hydrogenation decreased by a factor of 2. Holding the sulfide in flowing hydrogen at 450°C for 1 hr (after reaching temperature) gave a stoichiometry close to 2 : 1 and a further increase in specific rate constant, along with incremental sintering and loss LTOC (Run 3).

Effect of Hydrogen Sulfide Pretreatment

Table 2 summarizes the results of treatment in 15% H_2S/H_2. Included in the table are the specific rate constant for propene hydrogenation at 150°C, the apparent activation energy, BET surface area, LTOC, and the ratio of rate constant to oxygen

TABLE 2

Effects of H_2S/H_2 Pretreatment

Run No.	Pretreatment^a	k_s (150°C) (mol × 10^{10} cm^{-2} s^{-1})	E_{app} (kcal mol^{-1})	S(BET) (m^2 g^{-1})	LTOC (cm^3 (STP) g^{-1})	k_s/O_2 (mol mol^{-1} s^{-1})
2	H_2 to 450°C	0.71	3.7	13.9	0.63	0.35
4	H_2S/H_2, 450°C	0.033	11	35.9	0.44	0.060
5	H_2S/H_2. 450°C; H_2 to 450°C	0.46	5.1	17.6	0.65	0.28

[a] See text (Experimental) for details.

chemisorbed. Run 2 is the control (see Table 1) in which the molybdenum sulfide was subjected to TPR with H_2 to 450°C but was not H_2S treated. Run 4 is for a sample heated in H_2S/H_2 to 450°C and maintained at 450°C for 60 min before a He purge (15 min) at 450°C and cooling. In Run 5, the sample was treated as in Run 4 and cooled to room temperature, but TPR in H_2 to 450°C was then performed prior to measurement of activity and LTOC.

Pretreatment in H_2S/H_2 instead of pure H_2 (Run 4) had dramatic results, even though a He purge at 450°C preceded the activity and LTOC measurements. Sintering was very much less in H_2S/H_2 than in H_2: compare Runs 2 and 4. The specific rate constant for hydrogenation at 150°C was lower by a factor of about 20 in Run 4, and the apparent activation energy was sharply higher, by a factor of 3. Finally, the ratio of specific rate constant to oxygen chemisorption was decreased by a factor of 6, compared to the control run.

An attempt to reverse this effect of H_2S/H_2 pretreatment by adding on a treatment in H_2 to 450°C (Run 5) was only partially successful. The activity was largely, but not totally, restored; the activation energy decreased, though not to the level of the control; sintering again occurred because of the TPR in H_2; and the ratio of k_s/O_2 was increased, though not quite to that of the control sample.

DISCUSSION

Because of the low apparent activation energies for the samples reduced at 450°C (Table 1), consideration was given to the possibility of pore-diffusional limitation. The average pore diameters, calculated from the pore volume and surface area, were in the range 40–100 Å. SEM pictures showed that the catalyst particles were less than 40 μm. For pores of these dimensions (40 Å diam, 20 μm length), the effectiveness factor was found to be essentially unity under our reaction conditions (*37*). The activation energies of 3.7 and 2.8 shown in Table 1 are in reasonable agreement with the value of 3.2 kcal/mol reported by Lee and Butt for butene hydrogenation over sulfided S/Mo alumina catalysts.

The nonstoichiometric molybdenum sulfide resulting from ATTM decomposition is poorly crystalline and remains so after H_2 treatment at 450°C (*35*). A similar poorly crystalline material was prepared by Chang and Chan (*41*) by ATTM decomposition in H_2S at 350 or 400°C. From FTIR spectra they deduced that the sulfide contains nonstoichiometric sulfur but virtually no elemental sulfur. The nonstoichiometric sulfur may occur not only at the edges (*42*) but throughout the lattice (*43, 44*).

The specific activity for propene hydrogenation increases as nonstoichiometric sulfur is removed (Table 1), and the apparent activation energy decreases at the same time. The most dramatic change occurs after the second TPR peak has been traversed (Run 2, Table 1). Loss of surface area shows the same pattern: very little sintering occurs during the first TPR peak, but sintering is severe by the end of the second peak. Sintering at temperatures exceeding 250°C has been observed by others.

Reductive sulfiding in H_2S/H_2 is a common means of activating molybdena-alumina catalysts. In the present study of unsupported molybdenum sulfide, we find that treatment of the (already-prepared) sulfide with H_2S/H_2 (and no subsequent treatment with pure H_2) results in much less sintering than does H_2 treatment, lower loss of nonstoichiometric sulfur, much lower LTOC, much lower specific activity for hydrogenation, and a sharp increase in activation energy. The simplest supposition is that all of these phenomena are causally related; the key factor is probably a decrease in concentration of coordinatively unsaturated surface Mo ions when H_2S is continuously present in the gas stream. The effects were largely reversed by a subsequent treatment in pure H_2 (Run 5, Table 2); more stringent conditions for the H_2 treatment would probably make the results even closer to those for the reduced-only sulfide.

REFERENCES

1. Desikan, P., and Amberg, C. H., *Canad. J. Chem.* **42,** 843 (1964).
2. (a) Lipsch, J. M. J. G., and Schuit, G. C. A., *J. Catal.* **15,** 174 (1969); (b) Lipsch, J. M. J. G., Doctoral thesis, Technological University, Eindhoven, The Netherlands, 1968, reprinted by Climax Molybdenum Company, London, England.
3. Massoth, F. E., and Kibby, C. L., *J. Catal.* **47,** 300 (1977).
4. Voorhoeve, R. J. H., and Stuiver, J. C. M., *J. Catal.* **23,** 236, 243 (1971).
5. Farragher, A. L., and Cossee, P., *in* "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), p. 1301. North-Holland, Amsterdam, 1973.
6. Pratt, K. C., and Sanders, J. V., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" Elsevier, Amsterdam, 1981.
7. Sanders, J. V., and Pratt, K. C., *J. Catal.* **67,** 331 (1981).
8. Salmeron, M., Somorjai, G., Wold, A., Chianelli, R., and Liang, K. S., *Chem. Phys. Lett.* **90,** 105 (1982).
9. Tanaka, K., and Okuhara, T., *Catal. Rev.* **15,** 249 (1977).
10. Tanaka, K., and Okuhara, T., *J. Catal.* **78,** 155 (1982).
11. Okamoto, Y., Tomioka, H., Imanaka, T., and Teraniski, S., *J. Catal.* **66,** 93 (1980).
12. Okamoto, Y., Tomioka, H., Katoh, Y., Imanaka, T., and Teraniski, S., *J. Phys. Chem.* **84,** 1833 (1980).
13. Stevens, G. C., and Edmonds, T., *J. Less Common Met.* **54,** 321 (1977).
14. Stevens, G. C., and Edmonds, T., *J. Catal.* **71,** 230 (1981).
15. Tauster, S. J., Pecoraro, T. A., and Chianelli, R. R., *J. Catal.* **63,** 515 (1980).
16. Chianelli, R. R., and Tauster, S. J., *J. Catal.* **71,** 228 (1981).
17. Bahl, O. P., Evans, E. L., and Thomas, J. M., *Proc. R. Soc. A* **306,** 53 (1956).
18. Chadwick, D., and Breysse, M., *J. Catal.* **71,** 226 (1981).
19. Valyon, J., and Hall, W. K., *J. Catal.* **84,** 216 (1983).
20. Weller, S. W., *Acc. Chem. Res.* **16,** 101 (1983).
21. Weller, S. W., and Parekh, B. S., *J. Catal.* **47,** 100 (1977).
22. Millman, W. S., and Hall, W. K., *J. Catal.* **59,** 311 (1979).
23. Liu, H. C., and Weller, S. W., *J. Catal.* **66,** 65 (1980).
24. Tauster, S. J., and Riley, J. L., *J. Catal.* **70,** 230 (1981).
25. Bodrero, A., Bartolomew, C. H., and Pratt, K. C., *J. Catal.* **78,** 253 (1983).
26. Concha, B. E., and Bartholomew, C. H., *J. Catal.* **79,** 327 (1982).
27. Bachelier, J. Tiliette, M. J., Duchet, J. C., and Cornet, D. J., *J. Catal.* **76,** 300 (1982).
28. Vyskocil, V., and Tomanova, D., *React. Kinet, Catal. Lett.* **10,** 37 (1979).
29. Garcia Fierro, J. L., Soria, J., and Lopez Agudo, A., *Appl. Catal.* **3,** 117 (1982).
30. Uchytil, J., Beranek, L., Zahradnikova, H., and Kraus, M., *Appl. Catal.* **4,** 233 (1982).
31. Ratnasamy, P., and Sivasankar, S., *Catal. Rev. Sci. Eng.* **22,** 401 (1980).
32. Hall, W. K., *in* "Proceedings, Climax 4th International Conference, Colorado," (H. F. Barry and P. C. H. Mitchell, Eds.), p. 224. Climax Molybdenum Company, Ann Arbor, Michigan, 1982.
33. Bodrero, T. A., and Bartholomew, C. H., *J. Catal.* **84,** 145 (1983).
34. Fierro, J. L. G., Tejuca, L. G., Lopez Agudo, A., and Weller, S. W., *J. Catal.* **89,** 111 (1984).
35. Kalthod, D. G., and Weller, S. W., *J. Catal.* **95,** 455 (1985).
36. Kruss, G., *Liebig's Ann.* **225,** 1 (1884).
37. Kalthod, D. G., and Weller, S. W., *Chem. Eng. Commun.*, **39,** 323 (1985).
38. Satterfield, C. N., and Roberts, G. W., *AIChE J.* **14,** 159 (1968).
39. Lee, H. C., and Butt, J. B., *J. Catal.* **49,** 320 (1977).
40. Hishida, T., Uchijima, T., and Yoneda, Y., *J. Catal.* **17,** 287 (1970).
41. Chang, C. H., and Chan, S. S., *J. Catal.* **72,** 139 (1981).
42. Wildervanck, J. C., and Jellinek, F., *Z. Anorg. Allg. Chem.* **328,** 309 (1964).
43. Wentrcek, P. R., and Wise, H., *J. Catal.* **45,** 349 (1976).
44. Hou, P., and Wise, H., *J. Catal.* **78,** 155 (1982).

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