

CO Hydrogenation on Supported Molybdenum Catalysts: Effects of Support on Specific Activities of Reduced and Sulfided Catalysts

INTRODUCTION

Hydrogenation of CO on Group VIII metals (e.g., Co, Fe, Ni, and Ru) to produce methane and higher molecular weight hydrocarbons has been the subject of extensive research (1, 2). However, until recently, CO hydrogenation on molybdenum catalysts had received relatively little attention, probably because early studies (3) showed them to have only modest activity. Nevertheless, recent patents (4, 5) claim effective application of supported Mo catalysts to produce methane (4) and C₂-C₅ hydrocarbons (5) using feeds containing high concentrations of sulfur compounds in contrast to conventional catalysts (e.g., Co, Fe, Ni, or Ru) which suffer 3-4 orders of magnitude loss of activity within hours or days under comparable conditions (6, 7). Supported, potassium-promoted molybdenum catalysts were also recently reported (8) which exhibit greater than 70% selectivity to C₂-C₅ hydrocarbons and high resistance to poisoning by ppm levels of H₂S. Mo catalysts also maintain CO hydrogenation activity at low H₂/CO ratios (8, 9), while conventional catalysts lose activity.

A previous paper reported specific activity/selectivity data for unsupported Mo catalysts (9), while no such data were previously reported for supported Mo catalysts. The specific activities reported by Saito and Anderson (9) for unsupported Mo carbides, oxides, sulfide, and nitride were based on CO adsorption. Unfortunately, a correlation relating the number of active sites for CO hydrogenation to the amount of CO adsorbed on these catalysts was not demonstrated.

In a very recent study in this laboratory (10) a linear correlation was observed between O₂ adsorption on unsupported MoS₂ catalysts and activity for CO hydrogenation. Previous workers (11-17) have also demonstrated the utility of O₂ adsorption for the measurement of active hydrogenation sites of supported molybdenum oxide and sulfide catalysts. The objective of this study was to determine the effects of support on the specific CO hydrogenation activities and selectivities of reduced and sulfided molybdenum catalysts, active site densities of which were measured by O₂ adsorption.

EXPERIMENTAL

All catalysts prepared for this study (except unsupported MoS₂) contained 6.7 wt% Mo (10 wt% MoO₃). The preparation of these catalysts is described elsewhere (10, 11). Catalytic surface areas were measured by O₂ adsorption according to methods described elsewhere (11, 17). Surface and bulk phase compositions were measured by ESCA and X-ray diffraction spectroscopies as previously described (11). Values of O₂ adsorption uptake and BET surface area are listed in Table 1.

Catalysts were tested in a single-pass differential reactor system previously described (10). A 30% CO/H₂ mixture, prepared from Matheson-grade (99.99%) CO and 99.995% H₂, was passed through a heated molecular sieve/activated carbon trap to remove traces of iron carbonyl and other impurities and was combined with either pure H₂ or 66 ppm H₂S/H₂ to yield a 23-25% CO in H₂ (with or without 8-10 ppm H₂S) reactant mixture. A Perkin-

TABLE I

BET Surface Areas and O₂ Adsorption Uptakes of Supported Molybdenum Catalysts

Catalyst ^a	BET surface area ^b (m ² /g)	Net O ₂ uptake ^c following reduction (μmol/g)	Net O ₂ uptake ^c following sulfiding (μmol/g)
Mo/Al ₂ O ₃	180 ± 8 ^d	77 ± 2	47 ± 2
Mo/SiO ₂	134	89 ± 3	28 ± 1
Mo/CeO ₂	23	102	54
Mo/Carbon	537	350 ± 4	95 ± 5

^a Mo loading, 6.7 wt%.

^b Measured at 79 K with argon adsorbate on unsulfided catalyst; per gram of catalyst.

^c O₂ uptake measured at 195 K, corrected for support adsorption; per gram of catalyst.

^d Where means and standard deviations are shown, they were determined from the average of two or three independent measurements.

Elmer Sigma 1 gas chromatograph equipped with TCD, FID, and FPD detectors was used to analyze for CO, CO₂, C₁–C₅ hydrocarbons, H₂S, and COS. A portion of the H₂S (30–40%) reacted with CO to form COS before entering the reactor (18); however, the COS was not adsorbed on Mo catalysts under the conditions of this study.

A reaction temperature of 350°C was selected in order to minimize carbon formation while achieving a CO conversion sufficiently large to measure. Space velocities (measured at 25°C and 640 Torr) of 800 to 2000 hr⁻¹ and a reactor pressure of 140 kPa were chosen to keep CO conversions below 5% thereby minimizing mass or heat-transfer related disguises. All catalysts were crushed to a powder of 100–200 mesh in order to eliminate effects of pore diffusion on rates.

Previously calcined catalysts (11) were reduced *in situ* at 500°C for 18–20 hr and then tested for activity and selectivity in a sulfur-free reaction mixture for 20–25 hr followed by exposure to a reaction mixture containing 8–10 ppm H₂S for an additional 20 hr. Activity/selectivity data were likewise obtained over a period of 20–25 hr for catalyst samples which had been reduced at 500°C for 18 hr followed by sulfiding in 10% H₂S/H₂ at 400°C for 2 hr using a feed of 8–10 ppm H₂S and 23–25% CO/H₂.

RESULTS

Initial and steady-state CO conversions, initial rates of CO conversion (per gram of catalyst and in the form of CO turnover frequencies), and C₂₊ hydrocarbon selectivities (mole% product appearing as C₂₊ hydrocarbons) are listed in Table 2 for reduced and sulfided, supported Mo and unsupported MoS₂ catalysts.

The initial specific activity (turnover frequency) of Mo/SiO₂ is significantly higher relative to the other reduced, supported catalysts. Indeed, the order of decreasing specific activity is Mo/SiO₂ > Mo/Al₂O₃, Mo/C > Mo/CeO₂. During reaction at 350°C over a period of 20–25 hr, the activity of reduced Mo/SiO₂ decreased by 70% while the activities of the other reduced catalysts decreased by only 20–30%. Exposure to a reaction mixture containing 8–10 ppm H₂S for 20 hr (data are not shown), caused a significant further loss of activity (about 70%) in the case of Mo/SiO₂, while the activities of Mo/Al₂O₃ and Mo/CeO₂ were not affected and that of Mo/C was only slightly decreased. The observed relatively high resistance of Mo/Al₂O₃ and Mo/C to sulfur poisoning is in agreement with results obtained by Murchison *et al.* (8) for similar catalysts.

Initial specific activities (turnover frequencies) of MoS₂ and of sulfided Mo/Al₂O₃, Mo/SiO₂, and Mo/CeO₂ were the same within experimental error and significantly higher by factors of 6–8 than that for sulfided Mo/C. Indeed, with the exception of Mo/C, the mass-based activities of the freshly sulfided catalysts were found to correlate linearly with oxygen uptake (see Fig. 1). Compared to the freshly reduced catalysts, the activities of sulfided Mo/SiO₂ and Mo/C were significantly less, that of Mo/Al₂O₃ about the same, and that of Mo/CeO₂ significantly greater. Activities of the sulfided catalysts were generally quite stable during 20–25 hr of reaction.

The products of CO hydrogenation over reduced and sulfided Mo catalysts consisted of about 50 mole% hydrocarbons

TABLE 2
CO Conversions^a, Initial Specific Rates of CO Conversion, and Product Selectivities for CO Hydrogenation on Molybdenum Catalysts

Catalyst	Reduced (sulfur-free)					Presulfided ^b				
	CO Conversion %		Initial rate of CO conversion	Product selectivity	Initial rate of CO conversion	CO Conversion %		Initial rate of CO conversion	Product selectivity	Initial rate of CO conversion
	Initial	SS ^c	[mol/gS] × 10 ⁸	N _{CO} ^d × 10 ³ (s ⁻¹)		%C ₂₊ ^e	Initial	SS ^c	[mol/gS] × 10 ⁸	
6.7% Mo/Al ₂ O ₃	1.0	0.63	11	1.5	5	0.67	0.5	7.5	1.6	2
6.7% Mo/SiO ₂	4.2	1.4	57	6.4	12	0.27	0.2	3.6	1.3	7
6.7% Mo/CeO ₂	1.5	1.0	5.7	0.4	5	2.0	2.4	7.5	1.3	2
6.7% Mo/Carbon	6.2	4.9	50	1.4	11	0.03	0.02	0.9	0.2	0.5
MoS ₂ (unsupported)	—	—	—	—	—	1.3	2.72	3.4	1.1	3

^a Reaction conditions: 350°C, space velocity = 2000 hr⁻¹, 3:1 H₂/CO, 140 kPa.

^b Reactants contained 10 ppm H₂S; catalysts were presulfided in 10% H₂S/H₂ at 400°C for 2 hr.

^c After 20–25 hr of reaction.

^d CO turnover frequency, the number of CO molecules converted per site per second; site densities measured by O₂ adsorption.

^e Mole% of C₂₊ hydrocarbons in product; the product consisted of about 50 mole% C₁ and C₂₊ hydrocarbons and 50 mole% CO₂.

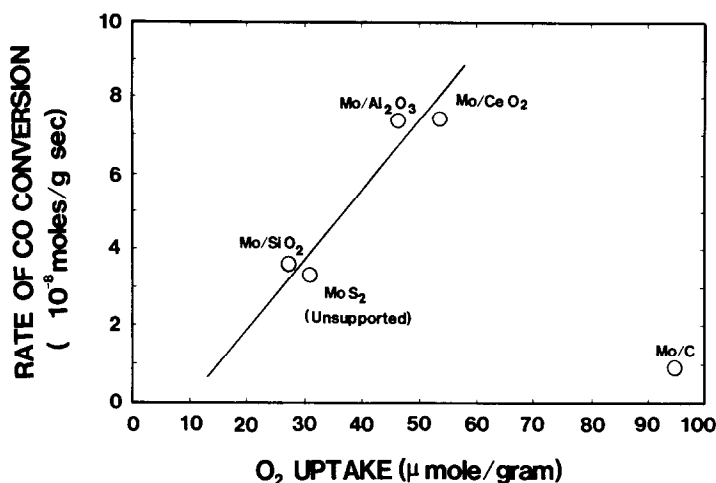


FIG. 1. Rate of CO conversion (mass based) vs oxygen uptake for freshly sulfided Mo catalysts.

(mostly methane, some ethane, and small quantities of C₃, C₄ hydrocarbons) and 50 mole% CO₂—no product water was observed in agreement with previous studies of CO hydrogenation on similar catalysts (8–10, 19). The C₂₊ selectivities were higher for Mo/SiO₂ than for other catalysts and higher for reduced catalysts compared to sulfided catalysts (see Table 2). They were quite consistent with values reported by Saito and Anderson (9) for Mo metal (in the case of Mo/SiO₂), MoO₂ (reduced catalysts), and MoS₂ (sulfided catalysts).

DISCUSSION

The data of this study provide evidence that the support greatly influences initial and steady state activities of reduced Mo catalysts, while the activities of sulfided Mo catalysts are, with the exception of Mo/C, independent of support and the same as for unsupported MoS₂. The variations in specific activity of the reduced catalysts with support reflect to a large degree the variations in chemical interaction of these supports with oxides of molybdenum (11).

There is evidence from previous studies (8, 20–25) and our companion adsorption, X-ray and ESCA study of the same supported Mo catalysts (11) that bulk and surface molybdenum phases in reduced cata-

lysts vary considerably with support. For example, it is known (21, 24) that reduction in H₂ at 500–600°C of Mo/Al₂O₃ yields primarily Mo⁴⁺ (MoO₂). However, reduction in H₂ at 500°C of Mo/SiO₂ and Mo/C results in formation of Mo metal and MoO₂ phases both in surface and bulk (8, 11). In the Mo/CeO₂ system, a highly dispersed MoO₃ phase (formed in calcination) is apparently only partly reduced to MoO₂ (11).

Previous studies (9, 26) have also demonstrated that the activity of reduced molybdenum for CO hydrogenation increases with decreasing oxidation state. Indeed, Saito and Anderson (9) reported that the order of decreasing activity for CO methanation was Mo metal > MoO₂ > MoO₃. They observed a 10-fold decrease in the methanation activity of Mo metal over a period of 100 hr; while the activity of MoO₂ was constant with time. Brenner and Hucul (26) observed a 10-fold decrease in the turnover number for Mo(0) over a period of 30 min and a further order of magnitude decrease over 17 hr which they attributed to oxidation of Mo(0) to MoO₂.

The high initial specific activity of reduced Mo/SiO₂ for CO hydrogenation observed in this study (Table 2) is undoubtedly explained by the fact that Mo(0) was the primary catalytic phase. The significant

loss of activity with time (Table 2) was probably due to oxidation of the surface by oxygen intermediates and water formed in the reaction. The lower initial specific activities of reduced Mo/Al₂O₃ and Mo/C for CO hydrogenation (Table 2) are consistent with the presence of a Mo(IV) surface oxide. The steady-state methane turnover numbers for reduced Mo/Al₂O₃ and Mo/C of 2 and 3 × 10⁻⁴ s⁻¹ (350°C) are in approximate agreement with the value of 3 × 10⁻⁴ s⁻¹ (250°C) reported by Brenner and Hucul for MoO₂/Al₂O₃ (26). However, they are about 10 times lower than the value of 4.3 × 10⁻³ s⁻¹ (350°C) reported by Saito and Anderson (9) for unsupported MoO₂ based on CO adsorption. This latter disagreement could be a result of support effects and/or significant differences in the surface site densities for O₂ and CO adsorptions on MoO₂. The significantly lower activity of reduced Mo/CeO₂ relative to the other reduced catalysts may be explained by less than complete reduction to MoO₂ as a result of strong molybdenum oxide-support interactions.

The close agreement of the initial CO turnover frequencies for sulfided Mo/Al₂O₃, Mo/SiO₂, and Mo/CeO₂ with that for unsupported MoS₂ indicates that the principal catalytic phase in these supported materials is also MoS₂ and that support-sulfide interactions do not significantly affect activity in these catalysts. The observed linear correlation of CO hydrogenation activity with oxygen uptake for the sulfided Mo catalysts (Mo/carbon excepted) indicates that the oxygen adsorption measures selectively the concentration of hydrogenation sites independent of the total surface area, which in these catalysts varied over a factor of 20.

The 30- to 50-fold lower activity of sulfided Mo/C relative to the other sulfided catalysts is quite unexpected. The most reasonable explanation for this behavior is poisoning of the surface by H₂S since in the companion study (11) it was observed that a large part of the H₂S had adsorbed on the

active carbon support, providing a large reservoir of H₂S for poisoning of the surface.

ACKNOWLEDGMENTS

One of us (Bernardo E. Concha) is very grateful to the National Council of Science and Technology (CONACYT, Mexico) for financial assistance during the pursuit of his master's degree. The authors gratefully acknowledge the support of the AMAX Foundation.

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Received October 6, 1983