

## MoS<sub>2</sub>-Catalyzed Methanation of CO with H<sub>2</sub>S<sup>1</sup>

Molybdenum disulfide is among the few methanation catalysts of CO that are unaffected by sulfur impurities (1, 2). Indeed, MoS<sub>2</sub> catalyzes H<sub>2</sub>S splitting, producing H<sub>2</sub> and S° above 400°C (3-5). The overall stoichiometry (6) of the MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>-catalyzed methanation reaction is 2CO + 2H<sub>2</sub> → CH<sub>4</sub> + CO<sub>2</sub>. Furthermore, when H<sub>2</sub>S (H<sub>2</sub>S/H<sub>2</sub> ≤ 10<sup>4</sup> ppm) is added to the feed gas, the methanation rate increases significantly.

The objective of our research was to investigate whether MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> directly catalyzes the methanation of CO with H<sub>2</sub>S, without added H<sub>2</sub>. Of special concern were the efficiency of the reaction, the effect of temperature, and the characteristics of the catalyst.

The preparation of MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> was a variation of a published procedure (6), except that the catalyst was not calcined at 500°C. 15.2 g of 3.2-mm activated γ-alumina pellets (80-100 m<sup>2</sup> g<sup>-1</sup>; Alfa) were immersed in 150 ml of aqueous 0.5 M ammonium molybdate (VI) (Aldrich) and then air dried at 100°C. Energy dispersive X-ray spectroscopy (EDS) of the treated Al<sub>2</sub>O<sub>3</sub> indicated that Mo was dispersed homogeneously throughout the support and that Mo/Al was 3.1 atom%, corresponding to 8.8 wt% of MoO<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub>. The MoO<sub>3</sub> was converted to MoS<sub>2</sub> in situ by reaction with H<sub>2</sub>S during the methanation of CO. Transmission electron imaging coupled with selected area electron diffraction and EDS analyses indicated that MoS<sub>2</sub> was present only on the Al<sub>2</sub>O<sub>3</sub> surface and not throughout the bulk support.

The reactant gases were introduced into a fix-bed flow reactor. Both reactant and

product gases were analyzed by a gas chromatograph equipped with a Teflon Haysep-C column and a stainless steel Carbosieve-S column for the respective separation of H<sub>2</sub>S and organics. Methane was detected by a flame ionization detector; other gases were monitored by a thermal conductivity detector.

Figure 1 displays a typical plot of the CH<sub>4</sub> production rate with time. After 2.5 h, the rate is seen to plateau. XPS studies of the catalyst indicated that the CH<sub>4</sub> production rate correlated with the conversion of MoO<sub>3</sub> to MoS<sub>2</sub>, implying that MoS<sub>2</sub> was the predominant active species. Other studies (6) support a similar conclusion about the methanation of CO in H<sub>2</sub>/H<sub>2</sub>S. After the methanation rate leveled off, the catalyst was found to consist of a mixture of MoS<sub>2</sub> and various oxides of molybdenum. The extent of converting MoO<sub>3</sub> to MoS<sub>2</sub> in H<sub>2</sub>S/H<sub>2</sub> is known (6, 7) to depend on the H<sub>2</sub>S concentration and the exposure time of MoO<sub>3</sub> to H<sub>2</sub>S. Both EDS and transmission electron diffraction showed the presence of hexagonal MoS<sub>2</sub> on the alumina, in agreement with the XPS results. TEM revealed that the MoS<sub>2</sub> was composed of 0.1 to 1.0 μm particles. Transmission electron diffraction patterns were consistent with MoS<sub>2</sub> particles having a microcrystalline structure. Dark field electron micrographs were formed using various regions (about 15° arc segments) of the (100)/(101) polycrystalline ring. Using this technique, the individual crystallites within the MoS<sub>2</sub> particle were imaged and found to be on the order of 1-10 nm. The micrographs also indicated that the MoS<sub>2</sub> particles were on the Al<sub>2</sub>O<sub>3</sub> surface and were not intimately incorporated into the support. XPS spectra showed S<sup>2-</sup> and small amounts of S° on the MoS<sub>2</sub> surface. No sulfur species were found on MoO<sub>3</sub>-free alumina that had been exposed to H<sub>2</sub>S and CO at 300°C. The XPS

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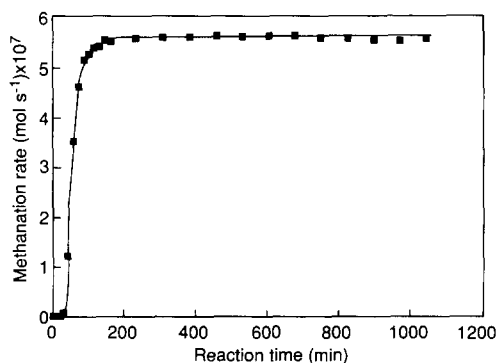
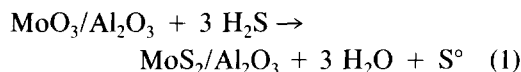


FIG. 1. Methanation rate dependence on time: reaction temperature, 350°C; total pressure, 1 atm; H<sub>2</sub>S,  $3.5 \times 10^{-6}$  mol s<sup>-1</sup>; CO,  $4.9 \times 10^{-6}$  mol s<sup>-1</sup>; space velocity, 45 h<sup>-1</sup>.

and electron diffraction data are consistent with the following reaction:



The presence of S<sup>2-</sup> on the MoS<sub>2</sub> surface is ascribed to H<sub>2</sub>S adsorption.

Both CH<sub>4</sub>/CO<sub>2</sub> and H<sub>2</sub>/COS were ~1 at 350°C. Furthermore, the omission of either H<sub>2</sub>S or CO eliminated H<sub>2</sub> production. These results suggest that CO and H<sub>2</sub>S underwent two simultaneous reactions on MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>:



The respective standard free energies are -24.9 and 1.2 kcal mol<sup>-1</sup>. Reaction (3) is slightly endergonic but is anticipated to be kinetically more favorable than reaction (2) because of its relative simplicity. In fact, COS/CH<sub>4</sub> was ~2.

Figure 2 shows that the CH<sub>4</sub> production rate did not pass through a maximum as the CO feed rate increased from 0 to  $3 \times 10^{-5}$  mol s<sup>-1</sup> at a constant H<sub>2</sub>S feed rate ( $3.5 \times 10^{-6}$  mol s<sup>-1</sup>), indicating that CO is more weakly bound to MoS<sub>2</sub> than H<sub>2</sub>S and does not easily displace H<sub>2</sub>S. At the reactor temperature, some dissociation of CO is expected (6). XPS studies indicate the pres-

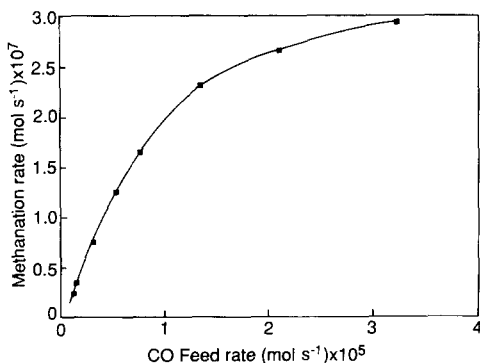


FIG. 2. Methanation rate dependence on CO feed rate: reaction temperature, 450°C; total pressure, 1 atm; H<sub>2</sub>S,  $3.5 \times 10^{-6}$  mol s<sup>-1</sup>.

ence of residue CH<sub>x</sub>. These observations suggest that CO and H<sub>2</sub>S react on the MoS<sub>2</sub> surface to form CH<sub>4</sub>. The CH<sub>4</sub> production rate plateaus at a CO/H<sub>2</sub>S of 12 at a constant H<sub>2</sub>S flow rate. In the plateau region, about 10% of the H<sub>2</sub>S and 1% of the CO are converted to CH<sub>4</sub> at 450°C and a space velocity of 270 h<sup>-1</sup>. At lower temperatures and space velocities, the conversion efficiency improves significantly, as discussed below.

Figure 3 displays a plot of the rate of CH<sub>4</sub> production between 100° and 600°C. The maximum rate ( $1.8 \times 10^{-7}$  mol s<sup>-1</sup>) occurs at 350°C. At this temperature, a space velocity of 50 h<sup>-1</sup>, and a CO/H<sub>2</sub>S of 1.6, about

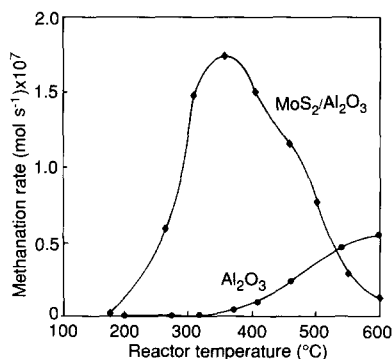


FIG. 3. Methanation rate dependence on temperature for MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>; total pressure 1 atm; H<sub>2</sub>S,  $3.7 \times 10^{-6}$  mol s<sup>-1</sup>; CO,  $5.9 \times 10^{-6}$  mol s<sup>-1</sup>; space velocity, 50 h<sup>-1</sup>.

50% of the H<sub>2</sub>S and 30% of the CO react to form CH<sub>4</sub>. Thus, decreasing the flow rate from 270 to 50 h<sup>-1</sup> and the temperature from 450° to 350°C produced a significant increase in the conversion efficiency. Below 350°C, no CH<sub>4</sub> production is seen on Al<sub>2</sub>O<sub>3</sub> in concurrence with the XPS results, showing no H<sub>2</sub>S adsorption on the support run at 300°C. Above 400°C, however, some CH<sub>4</sub> production on the support is observed. It is noteworthy that the rate of methanation on MoS<sub>2</sub> decreases above 350°C, whereas the reaction rate on Al<sub>2</sub>O<sub>3</sub> increases, implying that two mechanisms are operative above 350°C.

In conclusion, MoS<sub>2</sub> is found to catalyze the methanation of CO with H<sub>2</sub>S, without added H<sub>2</sub>. This reaction proceeds at high conversion efficiencies and its rate maximizes at about 350°C. Higher conversion efficiencies are expected with improved reactor design and catalyst preparation procedure and with further optimization of the reactant flow rates with temperature.

#### ACKNOWLEDGMENT

This work was supported by the Gas Research Institute.

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*Received November 16, 1989; revised July 17, 1990*

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