

## NOTES

## Fischer-Tropsch Synthesis over Supported Molybdenum Hexacarbonyl

During the last 5 years there has been growing interest in new types of catalysts derived from transition metal complexes with special interest focused on carbonyl complexes (1-5). Simultaneously there has been much research directed to the possible application of these materials to commercially important reactions, particularly more selective catalysts for Fischer-Tropsch synthesis (FTS) (5-10). An early report (11) showed that  $\text{Mo}(\text{CO})_6$  had no homogeneous activity for methanation or even olefin hydrogenation, an easily catalyzed reaction. However, it was later shown that when supported  $\text{Mo}(\text{CO})_6$  could be activated to yield substantially higher activity for these reactions than traditional catalysts (prepared by the reduction of a supported salt) of  $\text{MoO}_3$  (12-16). This note reports the first study of  $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$  under conditions conducive to FTS and demonstrates the improved activity and selectivity of this catalyst relative to  $\text{MoO}_3$ .

If present,  $\text{K}^+$  was added to the alumina (Conoco  $\gamma\text{-Al}_2\text{O}_3$ , Type Catapal SB) as  $\text{KNO}_3$  using the incipient wetness technique and the alumina was then dried at  $120^\circ\text{C}$  prior to calcination at  $500^\circ\text{C}$  (this "standard" alumina is about 28% hydroxylated,  $\bar{S} = 203 \text{ m}^2/\text{g}$ ). "Dehydroxylated" alumina (about 0.6% residual surface OH,  $\bar{S} = 125 \text{ m}^2/\text{g}$ ) was prepared by treating standard alumina at  $1000^\circ\text{C}$  for 1 h (this converts much of the  $\gamma\text{-Al}_2\text{O}_3$  to  $\delta\text{-Al}_2\text{O}_3$  (17)). Supported  $\text{Mo}(\text{CO})_6$  was prepared using the dry mixing (and rigorously air free) technique previously described (18). Following fixing the complex on the alumina by decomposition to  $\text{Mo}(\text{CO})_3(\text{ads})$  at  $100^\circ\text{C}$  in He (19), the catalyst was activated in  $\text{H}_2$  at  $500^\circ\text{C}$ .

Traditional  $\text{MoO}_3/\text{Al}_2\text{O}_3$  was prepared from  $(\text{NH}_4)_2\text{MoO}_4$  using the incipient wetness technique and reduced at  $500^\circ\text{C}$  in flowing  $\text{H}_2$ .

Reaction was carried out in a stainless-steel tubular reactor holding 0.7-1.0 g catalyst in a flow system. The catalyst was either activated *in situ* or prepared in a fused quartz reactor and then transferred to the stainless-steel reactor without exposure to air. Flows were controlled by a Brooks mass flow controller and pressure regulated by a Grove Mity-Mite back-pressure regulator. He and CO were purified with an Oxisorb cartridge (Scientific Gas Products) and the  $\text{H}_2$  was purified with a catalytic "oxygen removing purifier" followed by  $13\times$  molecular sieves (Matheson). Reaction products were analyzed by GC using several columns and peaks were integrated with a Hewlett-Packard Model 3388A digital integrator. Details of the experimental system will be published separately.

Table 1 shows the activities of both traditional and carbonyl-derived catalysts for FTS. The *formal* turnover frequency,<sup>1</sup> molecules reacting per unit time per metal atom in the catalyst (regardless of the dispersion), for  $\text{Mo}(\text{CO})_6/\text{dehydroxylated alumina}$  with 4%  $\text{K}^+$  is  $2 \times 10^{-2} \text{ s}^{-1}$ .  $\text{K}^+$  lowers the

<sup>1</sup> *Formal* turnover frequency is related to turnover frequency by the expression  $N_f = N(D)$ , where  $D$  is the fractional dispersion of a catalyst.  $N_f$  is a useful parameter for comparing activities when either dispersions are unknown or chemisorption appears to yield erroneous values. CO chemisorption at  $22^\circ\text{C}$  and 150 Torr on a catalyst of the type used in Table 2 and then cleaned in  $\text{H}_2$  at  $500^\circ\text{C}$  yielded a fractional dispersion of 0.005. Other data suggest that CO chemisorption significantly underestimates the true dispersion of these catalysts.

TABLE 1  
Activities of Mo Catalysts for FTS

Catalyst	Loading (% Mo)	% Conversion		Relative rate constant <sup>a</sup>	
		No K <sup>+</sup>	4% K <sup>+</sup>	No K <sup>+</sup>	4% K <sup>+</sup>
MoO <sub>3</sub> /standard alumina	5	28	17	1.00	1.00
Mo(CO) <sub>6</sub> /standard alumina	4	51	56	2.7	5.5
Mo(CO) <sub>6</sub> /dehydroxylated alumina	3	66	64	5.4	9.2

Note. Reaction conditions: 350°C, 355 psi, 1300 h<sup>-1</sup> GHSV, H<sub>2</sub>/CO = 1.

<sup>a</sup> Values of first-order rate constant relative to the value for MoO<sub>3</sub>/standard alumina.

activity of the traditional catalyst significantly more than for the carbonyl catalysts. Above 4% K<sup>+</sup> the activity of carbonyl catalysts drops slowly, being one-half as active with 15% K<sup>+</sup>.

Although the exact product distribution is somewhat dependent on the reaction conditions, a typical result is shown in Table 2. These catalysts yield close to 50 atom% of the product carbon as CO<sub>2</sub>, indicating equilibration of the water gas shift reaction. Thus, almost all of the oxygen in products leaves the reactor as CO<sub>2</sub> rather than H<sub>2</sub>O. For this reason the product distribution (carbon atom% selectivity) is given on a CO<sub>2</sub>-free basis. The C1 through C4 products obey Anderson kinetics (20) with a probability of polymerization of 0.37, but the C5 yield is somewhat less than predicted. In the absence of K<sup>+</sup> the olefin yield is greatly reduced and higher levels of K<sup>+</sup> modestly increase the olefin yield.

In most cases neither the conversion nor product distribution changes significantly during 20 h of reaction. Over the temperature range 300–425°C the activation energy is 18 kcal/mol and there is a negligible

change in the product distribution. From 115 to 765 psi (1 psi = 6.9 × 10<sup>3</sup> N m<sup>-2</sup>) the reaction is close to first-order in total pressure and the yield of CH<sub>4</sub> and LPG's (C2 through C4 hydrocarbons) drops slightly with increasing pressure.

The Bureau of Mines earlier studied FTS over a variety of Mo catalysts (21). Typical of the more active catalysts is No. L6117 consisting of 11% Mo/Al<sub>2</sub>O<sub>3</sub> which gave a conversion of 54% at 355°C, 309 psi, 292 h<sup>-1</sup> GHSV, and H<sub>2</sub>/CO = 1 corresponding to a formal turnover frequency of about 1 × 10<sup>-3</sup> s<sup>-1</sup> (or about 2 × 10<sup>-4</sup> s<sup>-1</sup> at the conditions of Table 1). The products were 68% CH<sub>4</sub>, 22% C2, and 10% C3 + C4. It is clear that the carbonyl catalyst is both significantly more active and results in less CH<sub>4</sub>. Murchison has recently reported improved Mo catalysts for synthesizing LPG's (22). A preferred catalyst used Saran carbon (with K<sup>+</sup>) as a support which aided in completely reducing the Mo during catalyst activation at 500°C in H<sub>2</sub>. This catalyst yielded 62% LPG's with a formal turnover frequency of about 1 × 10<sup>-3</sup> s<sup>-1</sup> at 400°C, 900 psi, 300 GHSV, and H<sub>2</sub>/CO = 1 (or

TABLE 2  
Product Distribution of Mo(CO)<sub>6</sub>/dehydroxylated Alumina (4% K<sup>+</sup>) for FTS

Conversion (%)	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	C5	C <sub>6</sub> <sup>+</sup>	LPG's
64	41.1	2.1	25.6	3.0	15.3	2.9	6.2	2.3	1.6	55

Note. Reaction conditions: as in Table 1.

about  $3 \times 10^{-5} \text{ s}^{-1}$  at the conditions of Table 1). After 500 h on stream XPS analysis showed that 53% of the Mo remained zero valent.

We suggest that the high activity of  $\text{Mo}(\text{CO})_6/\text{dehydroxylated alumina}$  is mainly due to the ability to initially prepare the Mo in an oxidation state close to zero. Reduction of  $\text{MoO}_3/\text{alumina}$  at  $500^\circ\text{C}$  yields primarily  $\text{Mo}^{4+}$  (23). Activation of  $\text{Mo}(\text{CO})_6/\text{standard alumina}$  at  $500^\circ\text{C}$  in an inert atmosphere yields an average oxidation state of  $\text{Mo}^{5+}$  due to reaction of the initially zero valent Mo with surface OH groups (24). As in the case of a traditional catalyst,  $\text{H}_2$  at  $500^\circ\text{C}$  reduces this material to mainly  $\text{Mo}^{4+}$  (19). However, this catalyst is several fold more active than the  $\text{MoO}_3$  catalyst of this study (and much more active than the Bureau of Mines catalyst). Both the use of a zero valent catalyst precursor and the use of dehydroxylated alumina appear important in achieving maximal activity (25, 26). The exact oxidation state of the Mo during reaction is uncertain. Some oxidation of  $\text{Mo}(\text{O})$  must occur since  $\text{Mo}(\text{CO})_6/\text{dehydroxylated alumina}$  is only modestly more active than  $\text{Mo}(\text{CO})_6/\text{standard alumina}$ . However, after 20 h of reaction at a conversion of 65% about 1500 molecules of water have been formed per Mo atom, but the catalyst still retains good activity. Thus, it appears that once synthesized in a low valent state the catalyst is at least modestly resistant to reoxidation to  $\text{Mo}^{4+}$  and  $\text{Mo}^{6+}$ , as also found by Murchison for  $\text{Mo}/\text{C}$  (22).

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