**Carbon Monoxide Hydrogenation over Molybdenum Carbide in a CSTR**

Patricia M. Patterson, Tapan K. Das, Burtron H. Davis  
Center for Applied Energy Research, University of Kentucky, 2540 Research Park Drive, Lexington KY 40511.

**Introduction**

Early transition metal carbides have been cited as potential substitutes for noble metal catalysts for a variety of reactions. Both molybdenum and tungsten carbides and nitrides have been shown to be promising catalysts for CO hydrogenation, hydrodenitrogenation, hydrodesulfurization and hydrolysis. This paper examines the preparation and catalytic activity of high surface area cubic molybdenum carbide for the Fischer-Tropsch reaction in a continuously stirred tank reactor (CSTR).

**Experimental**

The carbide was synthesized using the temperature programmed reaction procedure of Volpe and Boudart\(^1,2\), in which the high purity trioxide starting material was first nitrided in flowing NH\(_3\) followed by carbidization in a CH\(_4\)/H\(_2\) mixture (20.67% CH\(_4\) (v/v), balance H\(_2\)). In both cases the temperature was raised linearly using a low heating rate (0.6 K min\(^{-1}\)). For *ex situ* characterization purposes the samples were passivated in 1% O\(_2\) in helium at 498 K for 120 min. XRD analysis established that the sample was phase pure face-centered-cubic (fcc) molybdenum carbide. The carbide had a BET surface area of 95 m\(^2\) g\(^{-1}\). Elemental analysis yielded the generic formula of MoC\(_{0.4}\). The SEM images shown in Figure 1 demonstrate a pseudomorphism between the parent oxide and the product carbide indicating that the transformation from MoO\(_3\) to Mo\(_2\)N and subsequently to \(\alpha\)-MoC\(_{1-x}\) proceeded in a topotactic manner. A systematic abnormality in intensity distribution of the powder XRD peaks of the carbide was also found.

[Figure 1. SEM images of the parent MoO\(_3\) (right) and \(\alpha\)-MoC\(_{1-x}\) (left).]
Carbon monoxide hydrogenation using the molybdenum carbide catalyst was carried out in a slurry phase CSTR. Molten polywax was used as a startup solvent. The catalyst was activated prior to reaction in flowing carbon monoxide in situ at \( T = 493 \) K and \( P = 101 \) kPa for 24 h. Initial operating conditions used were \( \text{H}_2/\text{CO} = 2 \) (synthesis gas), \( T = 493 \) K, \( P = 2 \) MPa and space velocity = 5 SL h\(^{-1}\) g\(_{\text{cat}}\)\(^{-1}\). Conversion levels were determined by on-line gas sampling. Further details of the experimental conditions and reactor operation are available elsewhere\(^3\).

Results and Discussion
The conversion levels (mol\%) of the synthesis gas for the molybdenum carbide catalyst as a function of time on stream are shown in Figure 2, where changes in the reaction conditions are indicated by the arrows. Analysis of the gaseous products of the reaction showed that methane and carbon dioxide were the only carbon containing products, no liquid or solid products were produced under the reaction conditions. This indicates that in lieu of FT synthesis the predominant processes were the hydrogenation of CO to produce methane and water (\( \text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \)) and the subsequent reaction of the product water with CO to produce \( \text{CO}_2 \) and \( \text{H}_2 \), the water gas shift reaction (\( \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \)). The large amount of \( \text{CO}_2 \) produced instead of water, indicated that it is the CO rather than the carbide in the catalyst that was being hydrogenated. The \( \text{H}_2/\text{CO} \) ratio in the exit gas increased as the CO conversion increased also confirming the water gas shift activity as there was a net production of hydrogen as a result of the reaction.

Acknowledgements
This work was supported by U.S. DOE contract No. DE-FC26-98FT40308 and the Commonwealth of Kentucky.

References