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<td>A three year project to determine the feasibility of molybdenum carbide catalysts for the reforming of hydrocarbon fuels has been completed. As a result of this project, conditions for maintaining the stability of these catalysts under both dry and steam reforming methane have been determined. In particular it has been found that these catalyst can be kept stable by either operating at high temperatures, high pressures or by recycling CO and/or H₂. These conditions are all related to lowering gas-solid mass transfer rate. It has also been determined that tedious TPR catalyst synthesis techniques are not necessary to achieve either catalyst activity or stability. Because of these findings, it has also been possible to operate these catalysts at space velocities in excess of 30,000 hr⁻¹ and to therefore measure reaction kinetics for the first time. Finally, the sulfur tolerance of these catalysts has been studied by exposing them to a model sulfur compound (dimethylsulfide) during steam and dry reforming at sulfur concentrations as high as 500 ppmv. It concluded that sulfur reversibly chemisorbs on the catalyst surface, causing reduced but stable activity, and complete activity recovery can be obtained by simply removing sulfur from the feed.</td>
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LIST OF FIGURES

Figure 1 Oxidation Stability Diagram

Figure 2 Effect of Oxygen and Sulfur Concentration

Figure 3 Deactivation/Regeneration of Mo$_2$C Catalysts Exposed to Sulfur
PROBLEM STATEMENT

The goal of this project was to investigate the sulfur tolerance of molybdenum carbide catalysts, which are potential catalysts for the reforming of hydrocarbon fuels to produce hydrogen for fuel cell applications. However, in order to assess the sulfur tolerance of these catalysts, it was also necessary to first determine the process conditions under which these catalysts could be stabilized with respect to oxidation. The approach was to start with a simple hydrocarbon fuel (methane) and investigate catalyst stability in both dry and steam reforming and then evaluate the sulfur tolerance of the catalysts under otherwise stable conditions.

SUMMARY OF IMPORTANT RESULTS

As a result of this project, there were five separate areas where important results were obtained. These were:

- The importance of catalyst synthesis and catalyst surface area
- Fundamental criteria to stabilize the catalyst with respect to oxidation
- The importance of gas-solid mass transfer to the stability of the catalyst under dry and steam reforming conditions
- Determination of the kinetics of dry methane reforming over bulk Mo$_2$C catalysts
- Determination of the effect of sulfur on Mo$_2$C stability during dry and steam reforming of methane

Catalyst Synthesis and Surface Area  We have determined that the high surface areas produced by TPR catalyst synthesis methods are primarily due to excess carbon deposited during the synthesis. Furthermore, this carbon acts as nucleation sites for the deposition of additional carbon during reforming.

The role of catalyst pretreatment on the stability of Mo$_2$C catalysts in oxidative reforming environments were studied, using both the TPR and a solution-derived (SD) synthesis method, and compared to a low surface area commercial catalyst. Using a variety of techniques, including in-situ dynamic X-ray diffraction, the effects of various hydrogen pretreatment protocols were also evaluated, including catalyst thermal stability, oxidation resistance and susceptibility to coking. The high surface areas produced by the TPR and SD syntheses are attributed to the presence of excess synthesis carbon and, whereas the presence of excess synthesis carbon enhances thermal stability, it also appears to accelerate coking and promote oxidation. Comparative experiments of a TPR catalyst with a low surface area bulk catalyst produce similar activities. In addition it was also found that incomplete carburization during TPR synthesis, forms an oxycarbide and its acidity also promotes coking. Hydrogen pretreatment at 700 °C not only removes all excess synthesis carbon, but it also reduces the oxycarbide to Mo, which is easily
carburized under reforming conditions. Pretreatment at 600 °C, was largely ineffective and it is concluded that high temperature pretreatment is necessary to form the stoichiometric carbide, which is required for stability during reforming. In fact, as the temperature of the catalyst increases, the catalyst can be stabilized during reforming, even at atmospheric pressure, as long as temperatures are above 950 C for dry reforming and above 980 C for steam reforming.

**Catalyst Stability Towards Oxidation** We have discovered that stoichiometric feeds are, in fact, kinetically net oxidizing and deactivation will eventually occur if reforming kinetics are limiting. We systematically exposed the catalyst to various mixtures of reforming gas compositions, following the oxidation state of Mo2C by dynamic x-ray diffraction, and determined that oxidation can be prevented, even at low pressures, by insuring that a “stability ratio”, \( R_5 = \frac{P_{CO} + P_{H2}}{P_{H2O} + P_{CO2}} \), is greater than about 0.8 sol. The experimental results under a wide range of expected reforming gas compositions validate this criterion, and are shown in Figure 1. Gas compositions above the dashed line provide stable operation while compositions below the line lead to oxidation. This now explains the results reported by Sehested et. al. [2]. When they employed product gas recycle and found that the catalyst was stable even at 1 atm. pressure, they were in effect, increasing the stability ratio at the bed entrance.

**The Effect of Mass Transfer on Catalyst Stability** Early in the development of carbide catalysts for reforming, a research group at Oxford observed that carbide catalysts were stable at pressures of 8 bar but rapidly oxidized at atmospheric pressure sol. They attributed this to competitive kinetics between oxidation and carburization, concluding that carburization kinetics were more favorable at higher pressures. We have determined that higher pressures lower the mass transfer rates between the catalyst surface and the bulk gas sol. This has the effect of maintaining higher concentrations of the reforming product gases at the catalyst surface, thereby protecting the surface from oxidation. This also explains why previous investigators were unable to increase space velocities without causing catalyst oxidation. This is because previous investigators increased space velocity by increasing the gas flow over the same catalyst loading, thereby increasing the mass velocity as well (which also increases the mass transfer coefficient). However, when the space velocity is increased while maintaining low mass velocities, the catalyst is stable at space velocities of at least 30,000 h^-1. This is due to the effect of mass velocity on the mass transport of reaction products (H2 and CO) away from the catalyst surface. That is, at low mass velocities, the stability ratio (see Fig. 1) at the catalyst surface is greater than 0.8, and the catalyst does not oxidize. This also explains the effect of pressure noted by the Oxford group sol, because higher pressures lead to lower mass transfer coefficients.

**The Kinetics of Dry Methane Reforming over Bulk Mo2C Catalysts**

For the first time we have been able to obtain kinetic measurements of dry reforming over Mo2C catalysts sol. Up to now previous researchers were plagued by catalyst
deactivation whenever space velocities were raised and thus were not able to measure reforming reaction rates. Because we have learned how to keep the catalyst stable, we were able to obtain kinetic data at temperatures between 800 and 900°C, with CH4 and CO2 partial pressures from 0.15 to 0.32 bar and from 0.11 to 0.23 bar, respectively. Intrinsic kinetic measurements were made possible by co-feeding CO along with reactants at a constant CO:CO2 feed ratio of 3.0 in order to prevent oxidation of the Mo2C catalyst to MoO2. Methane conversion data as a function of inverse methane space velocity were obtained under conditions of negligible gas-solid mass transfer resistance and subjected to differential analysis. Partial pressure and rate data from all experiments were agglomerated and fit to a power law rate expression, which gave reaction the following rate expression for dry reforming of methane

\[
rate = 6.0 \times 10^7 e^{-\frac{41.200}{T}} P_{CH4}^{1.2} P_{CO2}^{0.7}
\]

The activation energy obtained in this temperature range was 41.2 kcal/mol, higher than reported values for supported nickel or noble metals for the same reaction. It is proposed that the rate data are consistent with a mechanism that involves a combination of carbidic carbon exchange and chemisorbed CO2, accounting for the high activation energy and the susceptibility of the catalyst to oxidation.

The Effect of Sulfur on Catalyst Stability

Once the stability issues of the carbide catalysts with respect to coking and oxidation were resolved, we were able to study the response of the catalyst to relatively high sulfur concentrations (up to 500 ppmv S as dimethylsulfide) during methane reforming. In addition to evaluating the effect of sulfur concentrations during methane reforming, we also examined the effect of oxygen levels, up to about 60% of auto thermal neutrality. Figure 2 shows the results of these experiments in terms of the carbon conversion as a function of oxygen concentration and at two sulfur levels, before and after sulfur exposure during experiments which were operating at steady state in a stoichiometric CH4:CO2 ratio. As can be seen, in the absence of oxygen (filled data points), the conversions immediately drop to 58% and 45% after exposure to 300 ppm and 500 ppm DMS, respectively. Although it is difficult to see from the plot, the conversions in all experiments, remain steady during the exposure to sulfur. However, during oxy-reforming with 9% oxygen, the steady state conversion drops only to 85%. The effect of oxygen can be seen more clearly by comparing this experiment at 370 ppm sulfur with the experiment at 300 ppm. In the latter case, no oxygen is present but its steady conversion in the presence of sulfur is only 58% as compared to 85% when oxygen is present. Figure 3 illustrates how the catalyst can also be regenerated when the feed sulfur is turned off. As can be seen, the conversions immediately return to their initial values. This and the fact that activity loss in the presence of sulfur is proportional to sulfur concentration and is steady, are all indications that sulfur is reversibly chemisorbed on the catalyst surface.

As a result of this study, the following conclusions have been drawn.
Mo$_2$C catalysts only partially deactivate in the presence of high sulfur concentrations but remain stable at lower conversions, dependent on the sulfur concentration in the gas.

It appears that partial deactivation is due to reversibly adsorbed sulfur and the degree of deactivation is proportional to the sulfur concentration.

The addition of oxygen to the reforming feed reduces the degree of conversion loss.

The catalyst can be quickly regenerated by returning to a sulfur-free feed or by exposing the catalyst to flowing hydrogen or helium. This is another indication that we are dealing with reversibly adsorbed sulfur.

LISTING OF MANUSCRIPTS

Papers Published in Peer Reviewed Journals


Papers Presented at National/International Meetings


Manuscripts Submitted to Peer Reviewed Journals

LaMont, D.C. and W.J. Thomson, “Dry Reforming Kinetics over a Bulk Molybdenum Carbide Catalyst”, submitted for publication, Chemical Engng Sci., 2004

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TITLE OF INVENTIONS


BIBLIOGRAPHY

APPENDICES - FIGURES

FIGURE 1

Oxidation Stability Diagram
FIGURE 2
Effect of Oxygen and Sulfur Concentration

FIGURE 3
Deactivation-Regeneration DMR/O2
400 ppm DMS