CATALYSTS FOR HYDROGEN PRODUCTION FROM METHANE

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Abstract

Bimetallic carbides such as Co,W,C have been synthesized and used for the reforming of methane to synthesis gas. These catalysts are active, selective and stable when they have been pretreated above 750°C. Reactivity experiments, coupled with characterization by XRD, show the effect of preparation procedure.

Introduction

Three processes exist for the production of hydrogen from methane: steam reforming, partial oxidation and dry reforming. The three main reactions are indicated below:

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2 \quad \text{(Steam Reforming) [1]}
\]

\[
\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 2 \text{H}_2 \quad \text{(Partial Oxidation) [2]}
\]

\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2 \text{CO} + 2 \text{H}_2 \quad \text{(Dry Reforming) [3]}
\]

Side reactions of importance include:

\[
\text{H}_2\text{O} + \text{CO} \leftrightarrow \text{H}_2 + \text{CO}_2 \quad \text{(Water-Gas Shift) [4]}
\]

Dry reforming produces a product (synthesis gas, or syngas) of a lower H2/CO ratio than the other two processes. However, there are advantages to this process, including the use of the greenhouse gas CO2 as a reactant.

Traditionally, a supported nickel catalyst has been used for dry reforming (1). However, this material deactivates rapidly, due to coke formation. Addition of alkali or alkaline-earth metals or passivation of the catalyst with, e.g., sulfur has been shown (2,3) to be effective. Noble-metal catalysts, e.g., Pt, have also been used. They are active and stable, but may be prohibitively expensive. Metal carbides are reasonably active and reasonably priced. (4).

Our work has concentrated on the use of bimetallic carbides as a way to modify the behavior if the carbides. Early work (5,6) used commercial material from Nanodyne. We have now started preparing the material in-house. In the current work, we report on a series of preparation and pretreatment techniques and show how they influence the reactivity behavior of these materials as well as their bulk characteristics.

Experimental

Catalyst Preparation. The procedure is similar to that of Polizzotti et al. (7,8) In brief, precursor solutions of ammonium triethylenediamine tungstate and cobalt chloride are mixed at room temperature. The tungstate solution is prepared by dissolving 14.5 g tungstic acid in 400 ml of a 1:1 aqueous ammonium chloride solution and 300 ml of ethylenediamine, followed by heating and stirring until the solution is clear. The cobalt solution is prepared by dissolving 13.8 g of the hexahydrate in 50 ml of distilled water. After mixing the two precursor solutions, the volume is reduced by 50% by evaporation. Pure cobalt triethylenediamine tungstate (Co(en)2WO4) is obtained by filtering, washing with acetone, and drying the filter cake in the hood for 24 h.

The bimetallic carbide is obtained by a temperature-programmed reaction (TPRx) of this material, using a mixture of CO and CO2 of specified ratio. The process is carried out at 1 atm in a fixed-bed reactor. In the TPRx procedure, the temperature is first ramped up to 650°C during the flow of 130 sccm of an equimolar mixture of Ar and H2, and the temperature held for 3 h. Then the mixture is flushed with Ar at 190 sccm for 0.5 h while the temperature is increased to 850°C. Last, the CO2/CO mixture flows through for 24 h with a total flow rate of 60(1+x) sccm, where x is the ratio CO2 / CO. The reactor is then purged by flowing Ar at 190 sccm, and cooled down to room temperature.

Catalyst Characterization. The material was characterized by N2 BET and by x-ray diffraction. XRD measurements were carried out both before and after reaction.

Reactor Setup. Reactions were performed in a stainless-steel reactor (SS 304L) with an outer diameter of 0.5 in and a length of 25 in, which was placed in an 18-in single zone furnace from Applied Test Systems. A stainless-steel sheathed thermocouple was inserted into the center of the catalyst bed to monitor and control the reaction range. The products were sampled immediately downstream at preset intervals using a Valco six-port gas-sampling valve. To prevent the outlet from heating up the valve beyond its operating range, a cooling system was added between the reactor outlet and the sampling valve, using circulating silicone oil at 90°C. The composition of the outlet gas was analyzed using an on-line Hewlett-Packard 5890 gas chromatograph (GC) equipped with a thermal-conductivity detector (TCD), which provided quantitative analysis for H2, CO, CH4, CO2, and H2O.

Typically 0.3 g of the catalyst sample was used for each test. The catalyst was pretreated by reducing with flowing hydrogen at 60 sccm for 1 h, followed by another hour of flushing with argon at 400°C. The reaction started once the pretreatment finished. The reactor was operated at 3.4 atm and 850°C with equal amounts of methane and carbon dioxide in the feed stream. The gas-hourly space velocity was kept constant at 9000 scc/hr/g cat. The conversions of the feed gases, the yields of the products, and the carbon balance, given by

\[
\text{Carbon Balance} = (\text{carbon out} - \text{carbon in}) / (\text{carbon in}) \quad [5]
\]

could then be calculated.

Results and Discussion

Characterization and reactivity data are discussed below for values of x equal to 0.1, 0.2, 0.5 and 0.75.

Catalyst Characterization. BET results indicate that the surface area of the fresh catalyst does not depend on the value of x. Typical surface area values were found to be 2-3 m2/g. This is approximately equal to the values for the Nanodyne materials, approximately 5 m2/g.

XRD patterns are shown in Figures 1-4 for the different catalyst materials. The major components present in the bulk are summarized in Table 1. Here Co,W,C represents an interstitial carbide with twice the amount of C present than in the bimetallic carbide Co,W,C.

Table 1. Bulk Components of Catalyst Materials as a Function of Pretreatment Conditions

<table>
<thead>
<tr>
<th>x = CO₂ / CO</th>
<th>Bulk Components</th>
</tr>
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<tbody>
<tr>
<td>0.1</td>
<td>Co,W,C, Co, WC</td>
</tr>
<tr>
<td>0.2</td>
<td>Co₃W₃C</td>
</tr>
<tr>
<td>0.5</td>
<td>Co₆W₆C</td>
</tr>
<tr>
<td>0.75</td>
<td>Co₆W₆C</td>
</tr>
</tbody>
</table>

Clearly the bulk components are dependent upon the ratio x (= CO₂ / CO), at least for values less than or equal to 0.5. Table 1 indicates that the relative amount of carbon present in the bulk compounds decreases, in general, as x increases, at least up to x = 0.5. This is consistent with the decreasing chemical activity of carbon, aC, as the CO₂/CO ratio decreases.

More importantly, Table 1 indicates that the bulk compounds present for the material made with x = 0.1 are those found in the Nanodyne catalyst after it reached its steady-state catalytic performance (6). This would seem to imply that the catalytically active material could be made directly by using in-house techniques.

Catalyst Reactivity and Stability. The catalytic performance of the bimetallic carbides prepared and characterized as described above is shown in Figures 5-7. While the individual behaviors are different, note that all three catalysts are characterized by an unsteady-state period of approximately 20 h, after which the catalyst is stable for at least the next 80 h. Clearly, the catalyst is still undergoing a solid-state reaction to

Figure 1. XRD spectrum from material made with x (= CO₂ / CO) = 0.1

Figure 2. XRD spectrum from material made with x (= CO₂ / CO) = 0.2

Figure 3. XRD spectrum from material made with x (= CO₂ / CO) = 0.5

Figure 4. XRD spectrum from material made with x (= CO₂ / CO) = 0.75

a more-stable phase, which is also the more catalytically active phase. The unsteady-state period is characterized by H2/CO ratios much higher than the expected (stoichiometric) value of 1 and a relatively low carbon balance of 70-80%. These observations are consistent with a laydown of carbon on the catalyst surface. Hence, in all cases, it would appear that carbon deposition leads to a more-stable, more-active phase on the catalyst surface.

From Table 1, the material prepared using x = 0.75 has the same bulk structure as the Nanodyne material. Hence it is worthwhile comparing the catalytic performance of these two materials. The Nanodyne material reaches its steady-state value in well under 20h (6), whereas the in-house material takes longer to approach steady state. The CH4 conversion is greater than the CO2 conversion in Figure 7, at least initially, whereas the reverse is observed (6) for the Nanodyne material, and at all times on stream. The ratio of H2/CO is significantly greater than the stoichiometric value (1.0) for the in-house material, especially during the unsteady-state period. All these observations imply that the in-house material results in greater carbon deposition and more water-gas shift products. The in-house material is also further from its final, catalytically active state than is the Nanodyne material.

As mentioned earlier, Table 1 indicates that the material prepared using x = 0.1 has the same bulk constituents found in the Nanodyne material (or the material prepared with x = 0.75) after it had reached its final, active state. Hence, one would expect the catalytic performance of the former material to require little or no time on stream to reach steady-state behavior, and for this behavior to be comparable to the steady-state behavior of the x = 0.75 (or Nanodyne) material. However, Figure 5 shows that steady-state behavior still requires 20 h on stream to be achieved, even though this amount is less than the comparable period for Figure 7. Clearly, even the catalyst that contains WC and Co in the bulk phase at the start needs pretreatment. Further, the H2/CO at unsteady state is much higher than the corresponding value in Figure 7. The CO2 conversion at steady state is somewhat greater than the CH4 conversion, implying less water-gas shift than for the x = 0.75 (or Nanodyne) material.

Finally, we consider the catalytic performance of the x = 0.2 material (Figure 6). The time to reach steady state in Figure 6 lies in between those in Figures 5 and 7. The catalytic performance in Figure 6 is more closely related to that in Figure 7 than that in Figure 5. This would appear to be counter-intuitive, given the values of x used in these three procedures and the bulk materials obtained from XRD. Again,
the nature of the catalytically active surface needs to be determined.

Figures 8 and 9 represent XRD patterns for materials after the reactions. For the $x = 0.75$ material (Figure 8), the bulk species after reaction are those obtained with the Nanodyne material, viz., WC, Co and C. For the $x = 0.1$ material (Figure 9), the bulk materials observed after reaction, in addition to C, are similar to those observed before, viz., Co$_3$W$_2$C, WC and Co, but in different relative amounts than before.

![Figure 8. XRD after reaction for material prepared with $x = 0.75$.](image)

![Figure 9. XRD after reaction for material prepared with $x = 0.1$.](image)

Conclusions

Bimetallic carbides such as Co$_6$W$_6$C have been synthesized and used for the reforming of methane to synthesis gas. These catalysts are active, selective and stable when they have been pretreated at 850°C. Reactivity experiments, coupled with characterization by XRD, relate the activity data to the formation of various chemical species in bulk. In all cases, there is an initial unsteady-state period characterized by carbon deposition and solid-state transformation of the material to a more catalytically active phase. However, it would appear that the connection between bulk structure and reactivity is ambiguous. Clearly, the surface nature of the catalyst needs to be obtained.

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References