

Bimetallic Carbide Catalysts for Methane Reforming

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“Dry” reforming is one of the processes used to obtain hydrogen from methane. The main reaction can be written as:

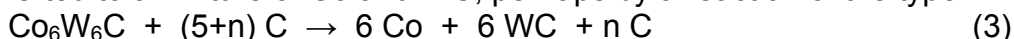


with the CO separated from the synthesis gas product in a subsequent step. Using CO₂ as a reactant (in place of H₂O used in steam reforming) renders the dry-reforming process of value in treating “stranded” natural gas, which generally contains CO₂ and which generally is found in areas of the world where water is not abundant. However, supported Ni catalysts, which are conventionally used in steam reforming, cannot be used for dry reforming as the catalysts deactivate due to coking, perhaps by a carbon-deposition side reaction of the type:



Noble-metal catalysts do not deactivate by this mode, but the costs may be prohibitive. Metal carbides are not as active as noble metals but are more economical, and deactivate less than supported Ni catalysts. Bimetallic carbides may improve catalytic performance even further.

We have shown¹ that a very active and stable catalyst can be produced by pretreating the commercially obtained η -carbide Co₆W₆C (Nanodyne, Inc.) with CH₄ and CO₂ at 850°C for a 24-hour period. Under these conditions, there is a net laydown of carbon on the catalyst, and the η -carbide is converted to a mixture of Co and WC, perhaps by a reaction of the type:



After pretreatment, the catalyst does not deactivate for at least 100 hours. At the end of the run, the material removed from the reactor is a mixture of Co, WC and C. In subsequent work,² we have shown that bimetallic carbides can be made in-house. The method of preparation can be modified to obtain materials with different x-ray diffraction (XRD) patterns. Specifically, this refers to the ratio of CO₂ to CO in the reducing stream flowing over the precursor Co(en)₃WO₄. When this ratio (termed *x*) equals 0.75, then Co₆W₆C is formed. The different materials made with different values of *x* have different catalytic properties but qualitatively similar x-ray diffraction patterns after reaction. But all these materials need to be held at high temperature for a period of time before they are active and selective for dry reforming.

In the present work, we have carried out a series of experiments with materials prepared by using values of *x* equal to 0.1, 0.2 and 0.75, in order to determine why the high temperature is needed to have the materials behave as suitable catalysts, and whether strategies can be used to carry out the reaction at lower temperatures. For these materials, the phases present in the bulk, as denoted by XRD, are shown in Table 1. Note that Co₃W₃C (= ½ Co₆W₆C₂) represents an extra carbon atom intercalated into the Co₆W₆C structure. This paper

Table 1. Bulk components of the catalysts with different values of *x*

<i>x</i>	<i>Bulk components</i>
0.1	Co ₃ W ₃ C+Co+WC
0.2	Co ₃ W ₃ C
0.75	Co ₆ W ₆ C

will concentrate on the results of the reactivity studies. Other characterizations of the materials, both before and after reaction have been reported elsewhere,³ those results will be used here to explain the phenomena.

In this work, the materials prepared in-house were exposed to reactants CH₄ and CO₂ at a series of increasing and decreasing temperatures. Reactions were performed in a stainless-steel reactor (SS 304L) with an outer diameter of 0.5 in. and a length of 25 in, 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 temperature. The products were sampled immediately downstream at the preset interval using a Valco six-port gas-sampling valve. To prevent the hot effluent gases from heating the valve to a temperature beyond its operating range, a cooling system of circulating silicone oil at 90°C was added between the reactor outlet and the sampling valve. The outlet composition 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 0.3g of the catalyst sample was used for each test. The catalyst was pretreated by reducing with flowing hydrogen at 60cc/min for one hour followed by another hour of flushing with argon at 400°C. The GC was switched on only after ensuring the flow of the Ar carrier gas through the column and TCD (30cc/min for each path). The reaction started once the pretreatment finished. The computer was preset to take samples at specified intervals and also to analyze samples for a certain time period. In the present work, the catalyst was kept at each temperature for at least 20h, then quickly heated or cooled to the next value. The temperature progression was:

$$700^{\circ}\text{C} \rightarrow 600^{\circ}\text{C} \rightarrow 850^{\circ}\text{C} \rightarrow 700^{\circ}\text{C} \rightarrow 600^{\circ}\text{C} \rightarrow 500^{\circ}\text{C} \rightarrow 700^{\circ}\text{C} \quad (4)$$

The reactivity results for the three materials are given in Tables 2-4. Here the carbon balance is defined as the relative difference between the amount of carbon in (by reactants) and the amount of carbon in the products measured leaving the system. Hence, carbon balance is a measure of both the accuracy of the measurements and the carbon laid down on the catalyst.

The results for the three materials are qualitatively similar. When the reaction temperature is first raised to 700°C (henceforth termed the “first 700°C stage”), the conversions and the yields are negligibly low. The carbon balance is relatively high, and the

Table 2. Reaction result with the catalyst made from $x = 0.1$

<i>Temperature (°C)</i>	<i>Conversion of CH₄ (%)</i>	<i>Conversion of CO₂ (%)</i>	<i>Yield of CO (%)</i>	<i>H₂/CO Ratio</i>	<i>Carbon Balance (%)</i>
700	4.45	7.71	3.99	0.127	97.88
600	1.63	1.61	0		98.38
850	72.09	68.45	66.75	0.989	96.50
700	28.43	34.13	26.42	0.795	95.10
600	9.15	13.29	9.01	0.467	97.76
500	4.12	4.55	2.24	0.307	97.86
700	27.66	34.50	27.05	0.759	95.92

Table 3. Reaction result with the catalyst made from $x = 0.2$

Temperature (°C)	Conversion of CH ₄ (%)	Conversion of CO ₂ (%)	Yield of CO (%)	H ₂ /CO Ratio	Carbon Balance (%)
700	3.84	4.14	1.88	0.233	97.89
600	2.46	1.43	0		98.06
850	80.53	76.84	67.58	1.079	88.92
700	29.55	35.51	28.35	0.799	95.78
600	8.83	12.49	8.56	0.473	97.88
500	4.35	4.63	2.25	0.297	97.76
700	27.69	33.83	26.77	0.774	95.97

Table 4. Reaction result with the catalyst made from $x = 0.75$

Temperature (°C)	Conversion of CH ₄ (%)	Conversion of CO ₂ (%)	Yield of CO (%)	H ₂ /CO Ratio	Carbon Balance (%)
700	3.63	5.37	2.03	0.223	97.52
600	2.84	2.88	0		97.14
850	78.77	73.67	63.73	1.113	87.54
700	29.01	35.93	27.72	0.788	95.21
600	9.15	13.86	8.92	0.489	97.38
500	4.32	5.59	2.19	0.315	97.23

H₂/CO ratio is low. At this temperature, there is apparently no deposition of carbon, and the catalyst is not in an active phase. At 600°C, conversions are not improved. However, when the reaction temperature reaches 850°C, the values of conversion and yield increase dramatically, and the carbon balance decreases. Carbon is deposited and the catalyst is in an active phase. When the temperature is decreased back to 700°C (henceforth, the “second 700°C stage”), the carbon balance goes back up, i.e., no carbon is being deposited. However, conversions and yields are significantly larger in magnitude than the values obtained with the catalyst during the first 700°C stage, i.e., before it was exposed to 850°C. In fact, the catalytic performance at 500°C after exposure to 850°C is comparable to the performance at the first 700°C stage. Even though no significant amounts of carbon are being deposited, the catalyst is still active. The performance is not as good as that at 850°C, but is remarkably better than that before it was exposed to 850°C. When the materials are brought back up to 700°C a third time (“the third 700°C stage”), the activities, yields and H₂/CO ratio are virtually indistinguishable from the parameters corresponding to the second 700°C stage. Clearly the catalyst is not deactivating and is in a stable phase.

XRD patterns were obtained from the $x = 0.75$ material after reactions at the first 700°C stage and the second 700°C stage. Similarly, SEM and EDS spectroscopy was carried out. The XRD patterns show³ the presence of CoWO₄, CO₆W₆C and WC after the first 700°C

stage, and only the active components Co, WC and C after the second 700°C stage. SEM micrographs³ show much more carbon present after the second 700°C stage than after the first 700°C stage. EDS measurements show large peaks of oxygen after the first 700°C stage, but after the second 700°C stage, the oxygen peaks are small and the carbon peaks are large.

This leads to the following working hypothesis for what goes on at the surface of the in-house materials. The CO₂-CO mixture flowing over the precursor leaves traces of oxygen on the surface of the materials. At low temperatures, less than 850°C, this surface oxygen is converted to oxides, rendering the material catalytically ineffective. At sufficiently high temperatures, the methane can react with the surface oxides or the surface oxygen and the bimetallic carbide to form Co, WC and elemental carbon, which constitute the active phase. Once these materials are formed, they are stable even at lower temperatures. This implies that the material can be an active, stable catalyst at relatively low temperatures, provided that it has been exposed to high temperatures earlier.

References

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