<table>
<thead>
<tr>
<th>Title</th>
<th>THE ROLE OF CARBON ON IRON SURFACE IN METHANATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Matsumoto, Hiroshige</td>
</tr>
<tr>
<td>Citation</td>
<td>長崎大学教養部紀要. 自然科学篇. 1981, 21(2), p.17-29</td>
</tr>
<tr>
<td>Issue Date</td>
<td>1981-01-31</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10069/16529">http://hdl.handle.net/10069/16529</a></td>
</tr>
</tbody>
</table>

NAOSITE: Nagasaki University's Academic Output SITE

http://naosite.lb.nagasaki-u.ac.jp
THE ROLE OF CARBON ON IRON SURFACE
IN METHANATION

Hiroshige MATSUMOTO
(Received September 17, 1980)

Abstract

The decomposition of carbon monoxide on a commercial fused iron catalyst for ammonia synthesis has been investigated in a flow system at 250°C under atmospheric pressures. The decomposition proceeded in accordance with the Boudouard reaction, disproportionation of carbon monoxide to carbon dioxide and surface carbon (Hägg carbide) with irreversible adsorption of carbon monoxide during an initial period. The rate of the disproportionation showed first-order dependence on the partial pressure of carbon monoxide.

The steady-state reduction of carbon monoxide with hydrogen to methane also has been carried out on the carbon-covered catalyst obtained by means of the Boudouard reaction at 250°C. With the increase in the amount of carbon on the surface, both rates of water and carbon dioxide formation decreased. On the other hand, the rate of methane formation was essentially independent of the amount of surface carbon up to 1.2 mmole/g, and then decreased linearly. In the methane formation the carbon-covered catalyst showed a period of induction which depended on the amount of surface carbon. From this evidence it was deduced that some of the surface carbon contributed not to the formation of a reaction intermediate but to the formation of an actual active site on the fused iron catalyst.

Introduction

For understanding the sequence of steps in methanation and Fischer-Tropsch synthesis on an iron catalyst, the effect of surface carbon species on the catalytic activity is of considerable importance. Anderson reported that large amounts of Hägg carbide were formed during Fischer-Tropsch synthesis over iron catalysts at high pressure (1). The iron carbide can be formed easily by means of carbon monoxide treatment of the iron catalyst at temperatures suitable for the Fischer-Tropsch synthesis. The carbide formation is accompanied by carbon dioxide formation according to Boudouard reaction:

\[ 2 \text{CO} + 2 \text{Fe} \rightarrow \text{CO}_2 + \text{Fe}_2\text{C}. \]

Thus the amount of the carbide can be estimated from the carbon dioxide formation in...
accordance with the above equation. However, it is normally assumed that the carbon dioxide produced in the Fischer-Tropsch reaction and in methanation partly comes from the water gas shift reaction and is therefore also a secondary product (2, 3). In the present work the carbon was deposited by exposing the iron catalyst to carbon monoxide prior to the catalysis.

In previous work (4), based on a transient experiment for the methanation of carbon monoxide over the same fused iron catalyst, I have reported that an intermediate on the surface was deactivated by an inert gas treatment. Since the amount of the reaction intermediate deactivated by the inert gas treatment corresponded to the amount of water removed from the surface during the inert gas treatment, I explained this deactivation process by the following reaction:

\[
\begin{align*}
\text{H}_2\text{O} & \quad \text{H}_2\text{O} \\
\text{C} & \quad \text{C} \\
\text{Fe} & \quad \text{Fe} \\
\downarrow & \quad \text{at 250 C in He}
\end{align*}
\]

Furthermore, the resulting carbon species on the iron catalyst had poor reactivity in comparison with the intermediate, but it was converted slowly to methane by hydrogen.

The objectives of the present work are to understand of carbon formation on a commercially available iron catalyst and to measure the catalytic activity of the carbon-covered iron for the reduction of carbon monoxide with hydrogen.

**Experimental**

The iron catalyst used in the present work was CCI fused magnetite catalyst for ammonia synthesis. Prior to use the catalyst was reduced in a hydrogen stream for a period of 48 hrs. at 450 C to get the largest surface area as shown in Table 1. The particle size of the catalyst used ranged from 250 to 300 μm. The X-ray diffraction pattern of this material revealed a good crystallinity of magnetite.

The apparatus used was a micro flow reactor similar to that used in the previous transient work (4). The unit consisted of 4-way switching valves connected in series to a reaction tube packed with 50 mg of the magnetite. A mass spectrometer was used for analysis of reactant and product gas. The reactor, made from stainless steel, was contained in an electric furnace of large heat capacity to keep the temperature constant. The maximum temperature variation over the reactor was less than 1 C.

The compositions of reactant and product were determined by a simple computer pro-
gram from the mass spectra, taking account of the cracking pattern for each pure component.

After the catalyst was reduced by hydrogen, it was treated with pure helium for 1 hr. at the reaction temperature. For studies of methanation rate, 10.02% carbon monoxide in hydrogen was introduced into the reactor via an activated carbon purifier to eliminate any carbonyl contaminant. The decomposition of carbon monoxide and the methanation were carried out at 250°C under atmospheric pressure.

The rate of product formation was calculated in the similar way to that in the previous work (4).

### Table 1 PROPERTIES OF THE FUSED IRON CATALYST USED

<table>
<thead>
<tr>
<th>Composition (wt. %)</th>
<th>BET Surface area Pretreat. temp. C m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₄ 96.5</td>
<td>400 12.5</td>
</tr>
<tr>
<td>Al₂O₃ 2.5</td>
<td>450 13.0</td>
</tr>
<tr>
<td>K₂O 0.6</td>
<td>500 12.3</td>
</tr>
<tr>
<td>SiO₂ 0.4</td>
<td>550 11.1 600 10.0 650 9.1</td>
</tr>
</tbody>
</table>

### Results and Discussion

**Interaction of CO and the Catalyst**

A typical result of the decomposition of carbon monoxide on the fused iron catalyst is shown in Fig. 1. The system was flushed with helium for 1 hr. at 250°C after hydrogen reduction at 450°C. Upon changing the flow to 10% carbon monoxide in argon, constant concentrations of carbon monoxide and carbon dioxide were observed in the outlet gas stream during the initial 100 minutes. After this period the rates of carbon monoxide consumption and carbon dioxide formation decreased with the time on stream. During the course of the reaction the ratio of carbon monoxide consumed to carbon dioxide formed remained constant at about 2. No appreciable amount oxygen in the gas phase was observed in this reaction. Essentially the same result was obtained if carbon monoxide was introduced immediately after hydrogen reduction without helium treatment. By the X-ray examination of the catalyst, the diffraction patterns of α-iron and that of Hägg carbide with composition approximating Fe₂C were observed in the early stage of the reaction. With the increase of the time on stream, the height of the diffraction pattern for the former decreased while that for the latter increased. The catalyst showed only the diffraction pattern of Hägg carbide after 1000 minutes of
treatment by carbon monoxide. No crystalline carbon material, such as graphite, was found even after 1500 minutes. Therefore, the main reaction of carbon monoxide decomposition on the fused iron catalyst is considered to be the disproportionation to carbon dioxide and Hägg carbide, and the amount of the carbon on the surface could be calculated approximately from the carbon dioxide formation. At higher temperatures, above 400°C, the main product in the reaction between iron and carbon monoxide is cementite, Fe₃C (5). However, Anderson et al. (1) confirmed the exclusive formation of the Hägg carbide during the Fischer-Tropsch synthesis on the similar fused iron catalyst at temperatures similar to those of the present work.

Bousquet et al. (6) and Tøttrup (5) reported that a constant rate of weight increase was observed after an initial rapid weight increase in thermogravimetric studies of the nickel-carbon monoxide system. They assumed that the initial weight increase was caused by adsorption of carbon monoxide on the nickel surface. In order to understand the initial stage of the carbon monoxide-iron interaction, 2% carbon monoxide in argon was used as feed. The result is shown in Fig. 2, where the amount of carbon is estimated by carbon monoxide consumption. Neither carbon monoxide nor carbon dioxide was observed in the outlet gas stream during a certain period, and then a constant consumption of carbon monoxide and a constant formation of carbon dioxide were observed. The absence of the reactant and of the product in the gas phase during the initial stage is presumably due to the adsorption of carbon monoxide on the surface, which corresponds to the initial rapid weight increase in the thermogravimetric experi-

![Graph: Amounts of CO consumption and CO₂ formation during the course of CO decomposition. (Concentration of CO in feed = 9.9%, temperature = 250°C, flow rate = 212 cc/min. g)
Fig. 2 Rates of CO consumption and CO₂ formation during the course of CO decomposition. (Concentration of CO in feed = 2.0%, temperature = 250°C, flow rate = 230 cc/min. g)

merits (5, 6). When the stream of carbon monoxide-srgon mixture flowing over the catalyst was suddenly changed to pure helium, neither carbon monoxide and nor carbon dioxide was detected in the helium stream. Thus, the adsorption of carbon monoxide seemed to be an irreversible adsorption which gives surface carbon and surface oxygen (5).

The amounts of surface carbon formed by the disproportionation and by the dissociative adsorption are cited in Table 2 for the catalyst treated by carbon monoxide during various periods. The amount of surface carbon associated with carbon dioxids formation was essentially proportional to the period of carbon monoxide treatment whereas that
without carbon dioxide formation was independent of the time on stream.

Table 2 CATALYST CARBURIZATION BY CO IN Ar*1 AND ITS METHANATION BY H₂ FLUSHING (m mole/g)

<table>
<thead>
<tr>
<th>CO treatment (min.)</th>
<th>Total C *2</th>
<th>C with CO₂ formation*3</th>
<th>C without CO₂ formation</th>
<th>CH₄ formed*4 by H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.25</td>
<td>0.07</td>
<td>0.18</td>
<td>0.16</td>
</tr>
<tr>
<td>10</td>
<td>0.36</td>
<td>0.16</td>
<td>0.20</td>
<td>0.27</td>
</tr>
<tr>
<td>20</td>
<td>0.54</td>
<td>0.33</td>
<td>0.21</td>
<td>0.42</td>
</tr>
<tr>
<td>40</td>
<td>0.88</td>
<td>0.68</td>
<td>0.21</td>
<td>0.87</td>
</tr>
<tr>
<td>70</td>
<td>1.39</td>
<td>1.20</td>
<td>0.19</td>
<td>1.43</td>
</tr>
</tbody>
</table>

*1 2% CO in Ar
*2 calculated from CO consumption
*3 calculated from CO₂ formation
*4 total methane formed at 250 and 450 C.

The graphs of carbon formation versus the time on stream from the experiments performed at various gas compositions are shown in Fig. 3, where the amount of surface carbon formed in accordance with the Boudouard reaction.
carbon was calculated from carbon dioxide formation. For each partial pressure of carbon monoxide in the feed gas, the amounts of carbon formed were proportional to the time on stream at the initial stage. The initial rate of the carbon formation from these slopes showed a good first order dependence on the pressure of carbon monoxide, as shown in Fig. 4. This result is consistent with that at higher temperatures (7). Thus, the initial rate in the disproportionation of carbon monoxide on the fused iron catalyst can be expressed by

\[ r = k P_{\text{CO}} S \]

where \( S \) represents the amount of the surface sites available for the reaction. The rate constant was estimated to be \( 1.4 \, \mu \text{ mole/} (\text{g. min. torr}) \) according to the above equation.

From these points of view, the main process of carbon monoxide decomposition on the iron catalyst at 250 °C may be explained by the following simple sequence. First, dissociative adsorption of carbon monoxide takes place on the iron surface to form Hägg carbide and surface oxygen. As the surface oxygen increases, it reacts with carbon monoxide to form carbon dioxide until a quasi-steady surface concentration of oxygen is obtained.

Wise and his co-workers reported (8) that in a carbon monoxide-nickel system the surface carbon can be rapidly and quantitatively converted to methane by hydrogen at 280
C. In order to confirm the reactivity of carbon species on the surface of the iron catalyst, pure hydrogen was passed over the catalyst carburized by carbon monoxide diluted with argon at 250 °C. The result is cited in the last column of Table 2. On exposure of the carburized catalyst to hydrogen, methane slowly formed. No higher hydrocarbons were observed in the outlet gas. However, only 50% to 70% of the surface carbon calculated from carbon monoxide consumption was converted to methane at 250 °C during a period of 300 min. exposure to hydrogen. After this period the temperature was elevated to 450 °C at a rate of 10 °C/min. in hydrogen. The maximum methane formation was observed approximately at 400 °C for the catalysts of various extents of carburization. The total amount of methane formed by the hydrogen flushing may be considered to correspond to the amount of total surface carbon within experimental error. Therefore, the carbon seems to be more strongly held on the iron surface than the nickel surface.

Reaction of CO and H₂ over the Carburized Catalyst

On introduction of 10% carbon monoxide in hydrogen to the freshly reduced catalyst at 250 °C, immediate formation of water and carbon dioxide was observed. On the other hand, formation of methane and other higher hydrocarbons, such as ethane and propane, was very slow during the initial period and gradually increased with the time on stream. The period required to get steady state of the hydrocarbon formation was approximately 65 min. in this condition. This induction period for formation of methane and of higher hydrocarbons decreased with increasing reaction temperature and the increase of carbon monoxide concentration in reactant gas.

The catalyst reduced by hydrogen at 450 °C was cooled down to 250 °C in a hydrogen stream and then treated in helium for 1 hr. After the helium treatment the catalyst was carburized by 4–10% of carbon monoxide in argon for certain periods. The activity tests for the carburized catalyst were carried out by 10% carbon monoxide in hydrogen at 250 °C under atmospheric pressure. The results for methane, water and carbon dioxide formation are shown in Fig. 5, Fig. 6 and Fig. 7, respectively. In comparison with the freshly reduced catalyst, the carburized catalyst showed a shorter period of induction for methane formation. This period decreased with increasing the amount of surface carbon up to 1.9 m mole/g. The catalyst covered by 2.7 and 3.3 m mole/g of surface carbon showed no substantial induction period. On the other hand, in the formation of water and of carbon dioxide no such a period of induction was observed for both the fresh and the carburized catalyst. At the initial stage of the reaction, the rate of water formation on 1.2 and 1.9 m mole/g carburized catalyst was higher than that on the fresh catalyst, whereas the rate of carbon dioxide formation decreased monotonously with the amount of carbon on the surface.
Fig. 5 CH$_4$ Formation on the catalyst covered with various amounts of carbon. Figures on the curves represent amounts of surface carbon in m mole/g.

Fig. 6 H$_2$O Formation on the catalyst covered with various amounts of carbon. Figures on the curves represent amounts of surface carbon in m mole/g.
Fig. 7 CO₂ Formation on the catalyst covered with various amounts of carbon. Figures on the curves represent amounts of surface carbon in m mole/g.

The steady-state rates of product formation are plotted against the amount of carbon on the catalyst in Fig. 8. The steady-state rates of water and carbon dioxide formation.

Figure 8 Relation between the steady-state rates of product formation and the amount of carbon on the surface.
strongly decreased with the increase of carbon on the surface. On the other hand, the steady-state rate of methane formation was essentially independent of surface carbon up to 1.2 m mole/g and then decreased with increasing surface carbon. Therefore, there seem to be at least two types of carbon species on the surface. One is a poison for methane formation and the other is not. There are, unfortunately, no satisfactory chemical methods for differentiating carbide from free carbon species on the surface.

Since surface carbon decreased the induction period (Fig. 5) and did not change the steady-state rate up to a certain amount of carbon (Fig. 8), it can be assumed that surface carbon contributes not to the formation of a reaction intermediate but to the formation of actual active sites on the iron catalyst. This idea is supported by the fact that the hydrogenation of surface carbon gave methane as the only hydrocarbon product whereas small but definite quantities of ethane and propane were observed in the reaction product with carbon monoxide and hydrogen interaction. Also, the rate of methane formation from surface carbon was much slower than that in the steady state of the catalysis (4). Anderson et al. (1,2) reported that α-iron was converted to Hägg carbide during the Fischer-Tropsch synthesis by a fused iron catalyst at high pressures. Examination by X-ray diffraction of the catalyst used for the experiment of Figs. 5, 6, 7 and 8 showed the presence of only two crystalline iron phases, α-iron and Hägg carbide. No appreciable difference in X-ray diffraction patterns was observed between the carbon-covered catalysts produced by carbon monoxide treatment and the catalyst after use for the methanation reaction.

When the feed to the catalyst in the steady state was changed to helium and then to hydrogen for short periods at 250 C, switching back to the reaction mixture produced no induction period in methane formation. These catalysts treated by helium and hydrogen showed substantially the same patterns of Hägg carbide and of α-iron in the X-ray examination. On the other hand, when the catalyst in the steady state was treated by hydrogen for 24 hrs. at 450 C to remove carbon species on the surface, the catalyst regained the same induction period and activity as the freshly reduced catalyst. In the previous work (4), since the amount of a reaction intermediate deactivated by an inert gas treatment closely corresponded to the amount of water removed from the surface, it was deduced that an intermediate of enol type on the iron was dehydrated to an inactive carbon species.

Conclusions

The essential reaction steps in the methanation by the iron catalyst will be summarized here with regard to the reaction intermediate and to the active sites on the surface.

1. When the reaction mixture is passed at 250 C over the catalyst freshly reduced in H₂ at 450 C, an overshoot in H₂O and CO₂ formation occurs (Figs. 6 and 7). If α-iron were the active site for methanation and Fischer-Tropsch synthesis, an over-
shoot in methane and higher hydrocarbons would be expected. No such immediate production of \( \text{CH}_4 \) occurs (Fig. 5). As the CO/\( \text{H}_2 \) mixture gradually transforms the iron surface, sites are produced where CO is not so strongly adsorbed, so that the adsorbed CO and H can interact to form the enol intermediate leading to methane and higher hydrocarbons. I have shown in my previous work (4) that this intermediate is dehydrated by helium at 250 C to an inactive form of carbon (carbide).

2. Deliberate addition of carbon to the surface of the catalyst by the Boudouard reaction prior to exposing the catalyst to CO/\( \text{H}_2 \) reduces and eventually eliminates the induction time for \( \text{CH}_4 \) formation (Fig. 5). During the induction period of the CO/\( \text{H}_2 \) reaction the sites for methanation / Fischer-Tropsch reaction build up to a steady-state level. However, if carbon addition is continued to higher levels via the preliminary Boudouard reaction, the resulting carbon becomes an inhibitor (Figs. 5 and 8). This carbon (carbide) is only slightly reactive and can be removed partly by reduction in \( \text{H}_2 \) at 250 C and completely by reduction in \( \text{H}_2 \) at 450 C. Thus the active sites are probably iron altered by some carbide bonds and not the carbon or carbide atoms themselves, although some of the carbon is reactive with \( \text{H}_2 \) at 250 C, forming \( \text{CH}_4 \) but no higher hydrocarbons.

The preceding ideas are summarized as follows:

i) Formation of the active sites on the iron catalyst.

\[
2 \text{CO} + 2 \text{Fe} \rightarrow \text{CO}_2 + \text{Fe}_2\text{C}
\]

In this step carbon monoxide adsorbs dissociatively on the iron surface to give Hägg carbide and surface oxygen (Fig. 2). The latter reacts with carbon monoxide to carbon dioxide (Fig. 3).

ii) Formation of the reaction intermediate species

\[
\text{H}_2 + \text{CO} + \text{Fe}_2\text{C} \rightarrow \ \begin{array}{c}
\text{H} \\
\text{OH}
\end{array} \quad \begin{array}{c}
\text{C} \\
\text{Fe}_2\text{C}
\end{array}
\]

Here, the intermediate species is formed by the interaction between adsorbed hydrogen and carbon monoxide (8, 9, 10) on the Hägg carbide.

iii) Formation of the main products from the intermediate.

\[
2\text{H}_2 + \ \begin{array}{c}
\text{C} \\
\text{Fe}_2\text{C}
\end{array} \rightarrow \text{CH}_4 + \text{H}_2\text{O} + \text{Fe}_2\text{C}
\]

The intermediate reacts with adsorbed hydrogen and with the neighboring intermediate on the surface to methane and to higher carbon-number species, respectively (8,9). In the absence of hydrogen, the intermediate is dehydrated to an inactive carbon species on the surface.
THE ROLE OF CARBON ON IRON SURFACE IN METHANATION

References


(4) Matsumoto, H., This Journal, 21, (2) 5 (1981).