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SYNTHESIS GAS CONVERSION ON CARBON SUPPORTED IRON CATALYSTS AND THE NATURE OF DEACTIVATION

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ABSTRACT

The quality of Fe/C catalysts for the production of C2 and C3 olefins from synthesis gas was investigated along with the nature and kinetics of deactivation. Carbon supported iron catalysts show remarkable high selectivities to lower olefins. However, they inherently possess a strong tendency to form graphitic carbon in the form of fibers. A very active iron carbide phase interacting with the carbon support is thought responsible for these features.

INTRODUCTION

Catalytic conversion of coal derived synthesis gas is an important step in the conversion of coal to hydrocarbons. From the economic point of view the production of short chain olefins is attractive, as these are the most valuable bulk hydrocarbons. Success in developing such a process demands the invention of new catalysts and appropriate reaction conditions to achieve activity, selectivity and an acceptable life time of the catalyst.

Unsupported, promoted iron catalysts are the only known commercial catalysts, used primarily for the production of automotive fuels [1,2]. Improvement in activity and selectivity for short chain products, excluding methane is a challenging desire for new applications.

Carbon supported catalysts are promising in this respect, considering recent publications of Vannice et al. [3-6]. Remarkably high activities and olefin to paraffin ratios were noticed for these catalysts, while the stability seemed satisfactory.

Deactivation is a serious problem in Fischer Tropsch catalysis. In case of industrial iron catalysts the main cause of deactivation is the gradual accumulation of carbon deposits, eventually resulting in physical breakdown of the catalyst.

For nickel catalysts this carbon formation has been intensively studied, including reaction kinetics and morphology of the carbon formed [7-11]. Intentional carbon deposition on iron by means of CO disproportionation or hydrocarbon decomposition has also been studied [12-14], but studies in connection with Fischer
Tropsch synthesis have not been reported. The purpose of this study is a more profound investigation of the qualities of Fe/C catalyst for the production of C₂ and C₃ olefins and of the nature and kinetics of its deactivation.

EXPERIMENTAL METHODS
Catalyst preparation

The catalysts were prepared by the incipient wetness method. Catalysts with a metal loading of 4-5% were obtained by a single impregnation of the support with an aqueous solution of iron(III) nitrate (Merck), followed by 2 hours drying at 300 K under vacuum and calcining at 723 K for 16 hours in flowing nitrogen. The catalysts were then cooled down to room temperature and stored in vacuum to prevent water uptake from the atmosphere. Catalysts with metal loadings of about 9% were prepared by repeated impregnation, drying and calcining, using the same iron nitrate solution. Three commercial activated carbon supports were used: RO-0.8 (900 m² g⁻¹) and R1-E (1250 m² g⁻¹) both from NORIT, and C-35 eponite (1250 m² g⁻¹) from DEGUSSA.

Kinetic measurements

The kinetic measurements were carried out in a 6 mm inside diameter tubular quartz reactor, containing a fixed bed of approximately 0.5 g of catalyst, particle size 0.2 < dp < 0.6 mm. The reactor was heated in an electric furnace. A chromel/alumel thermocouple was inserted into the catalyst bed for accurate measurement of the reaction temperature. The reactor was operated at atmospheric pressure. The gases used, He (Hoekloos, purity 99.995%), H₂ (Hoekloos, purity 99.9%) and CO (Matheson, purity 99.5%) were separately purified over a reduced copper catalyst (BASF R 3-11) at 423 K followed by a 5A molecular sieve (Union Carbide) at room temperature.

For each synthesis experiment a fresh catalyst was loaded and reduced in flowing hydrogen (50 ml min⁻¹) for 16 hours at 723 K, after which the reactor was cooled down to the desired synthesis temperature. Before admitting synthesis gas the reactor was flushed with helium to remove the excess of hydrogen. The hydrocarbon product distribution was measured on-line using two GLC's containing a n-octan/Poracil-c and a phenylisocyanate/Poracil-c column respectively. Water and carbon dioxide were continuously monitored using a dewpoint indicator and an infrared monitor.

Thermogravimetric analysis

The experiments were carried out in a thermobalance (Dupont 950) at atmospheric pressure. The sensitivity of the system was about 5 μg. The temperature was controlled within 2 K and measured with a thermocouple just above the catalyst.
Figure 1 Performance of 4.4% Fe/RO-0.8 (closed marks) and 4.4% Fe/R1-E (open marks) with respect to the formation of C₁-C₃ hydrocarbons.
(a) Activity versus temperature at H₂/CO=1
(b) Selectivity versus H₂/CO ratio at 673 K
Components depicted: CH₄(o,a), C₂+ (▲,▲), C₂+C₃(r,m)

A quantity of 50 mg of the catalyst was exposed to mixtures of CO, H₂ and He. The individual gases were purified as described above. The change in catalyst weight was recorded at constant temperature.

Characterization of the catalyst
The exact values of the metal loading of the catalysts were determined by atomic absorption spectroscopy. The average particle size was derived from XRD line broadening and TEM pictures, resulting in an estimate of 60-100 Å. Chemisorption of H₂ or CO at room temperature did not give meaningful results with respect to the metal surface due to excessive adsorption on the carrier. These properties of activated carbon are well known and were confirmed by experiments with unloaded material.

BET surface area and pore size distribution were determined by N₂ adsorption and Hg-porosimetry. Surface areas in the range of 900-1250 m² g⁻¹ were found (see 2.1), of which more than 90% is present in micropores. These data are in good agreement with the specifications of the manufacturers.

Data analysis and calculations
The data, obtained from the GC equipment were converted into molar concentrat-
ions. Multiplication with the actual flow lead to production rates for each component in \( \text{umol s}^{-1} \). These values were used to calculate "activities" \( A_i \) expressed in equivalent amounts of carbon atoms converted per gram per second.

The total hydrocarbon activity \( A_{HC} \) was defined as the total number of carbon atoms ending up in hydrocarbons (C\(_1\)-C\(_6\)) per gram iron per second.

Selectivities \( S_i \) were defined as the ratio of \( A_i \) to \( A_{HC} \).

RESULTS

**Catalyst reduction**

The observations made during the 16 hours reduction period at 723 K deserve special attention. During the first hour of this treatment the formation of some ethane and propane was observed besides methane and water. After this first hour the reaction goes on, but with methane as the only product. Apparently the production of hydrocarbons is due to catalytic gasification of the support. The reaction does not occur on the pure, iron-free support, and the gasification rate is higher at a higher metal loading.

The total weight loss of the catalyst, calculated from the carbon content of the hydrocarbons produced, amounted to 2-8\%. The total production of water approximated the theoretical value calculated for complete reduction of Fe\(_2\)O\(_3\) to metallic iron for 95\%.

**Synthesis gas conversion; activity and selectivity**

Experiments with synthesis gas were carried out at various conditions with respect to temperature, \( \text{H}_2/\text{CO} \) ratio and time on stream, with particular attention for the selectivities towards C\(_2\) and C\(_3\) olefins.

As to the temperature an optimum was found at approximately 670 K. A typical example is given in Figure 1a. Obviously olefins are among the primary products of the reaction. Their formation appears to demand a relatively high activation energy, as temperature increase initially favours the olefin formation. Above 770 K, however, methane becomes predominant as thermodynamics dictate its formation at the cost of higher hydrocarbons.

The \( \text{H}_2/\text{CO} \) ratio expectedly had a rather drastic effect on the olefin selectivity, as shown in Figure 1b. Increasing the \( \text{H}_2/\text{CO} \) ratio (at constant CO partial pressure and constant total flow) strongly increases the reaction rate, but lowers the olefin selectivity due to an increase in the hydrogenation capacity at the catalyst surface, yielding more methane and paraffins.

To compare the results of the various catalyst we prepared, relevant data are collected in Table 1, together with some data of Fe/C catalysts reported by Vannice et al. [3-6]. The enhanced olefin selectivity and the high activity we found for these catalysts are in line with the results of Vannice. Comparing the 4.4\% and 8.8\% metal loading one observes that the activity increases almost proportionally with
The best selectivities towards $C_2$ and $C_3$ olefins were obtained with the 4.4% Fe/RO-0.8 catalyst at 673 K and $H_2/CO = 1$, showing an olefin paraffin ratio of 9 and a relatively low methane production. The performance of the Fe/C-35 catalyst shows a much poorer performance, because of enhanced methane formation and a strong and rapid deactivation. The performance of the Fe/RI-E catalysts shows minor differences with Fe/RO-0.8.

**Deactivation**

As low $H_2/CO$ ratios are required to achieve high selectivities one may expect that deactivation by carbon deposition can be problematic. Catalyst deactivation was therefore studied in some detail. Figure 2 shows the hydrocarbon activity versus time profile for the best catalyst. The $CO_2$ and water curves are also depicted as they deserve special attention. Figure 3 shows the corresponding selectivity pattern. These figures tell us the following with respect to hydrocarbon synthesis:

(a) The maximum activity is reached at once; there is no activation period i.e. the active sites have been formed during reduction with hydrogen.

(b) The activity gradually decreases to approximately 25% of the initial activity.
TABLE 1
Selection of results of various catalysts in the fixed bed flow reactor

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature (K)</th>
<th>H$_2$/CO ratio</th>
<th>Conv. (%)</th>
<th>Activity $\mu$log.m$^{-1}$s$^{-1}$</th>
<th>Selectivity (C atom %)</th>
<th>$\frac{C_2+C_3}{C_2+C_3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4% Fe/RO 0.8</td>
<td>673</td>
<td>1:1</td>
<td>2.3</td>
<td>6.8</td>
<td>18 31 5 30 2 9 5 --</td>
<td>9.0</td>
</tr>
<tr>
<td>4.4% Fe/RO 0.8</td>
<td>673</td>
<td>2:1</td>
<td>5.8</td>
<td>14.2</td>
<td>22 20 11 26 6 6 5 3</td>
<td>2.7</td>
</tr>
<tr>
<td>4.4% Fe/RO 0.8</td>
<td>673</td>
<td>3:1</td>
<td>8.3</td>
<td>16.9</td>
<td>23 15 12 23 8 8 8 3</td>
<td>1.9</td>
</tr>
<tr>
<td>8.8% Fe/RO 0.8</td>
<td>673</td>
<td>1:1</td>
<td>4.2</td>
<td>6.9</td>
<td>26 23 11 24 3 7 3 3</td>
<td>3.3</td>
</tr>
<tr>
<td>4.4% Fe/R1 E</td>
<td>673</td>
<td>1:1</td>
<td>3.2</td>
<td>7.0</td>
<td>21 27 6 22 3 10 8 3</td>
<td>5.4</td>
</tr>
<tr>
<td>8.8% Fe/R1 E</td>
<td>673</td>
<td>1:1</td>
<td>5.9</td>
<td>7.4</td>
<td>25 25 9 19 9 7 3 3</td>
<td>2.4</td>
</tr>
<tr>
<td>4.4% Fe/C35</td>
<td>673</td>
<td>1:1</td>
<td>1.4</td>
<td>3.1</td>
<td>26 16 4 13 2 11 11 16</td>
<td>6.5</td>
</tr>
<tr>
<td>4.4% Fe/RO 0.8</td>
<td>523</td>
<td>1:1</td>
<td>0.7</td>
<td>2.0</td>
<td>18 20 9 30 7 13 2 --</td>
<td>3.1</td>
</tr>
<tr>
<td>4.4% Fe/R1 E</td>
<td>523</td>
<td>1:1</td>
<td>1.3</td>
<td>2.1</td>
<td>19 10 8 20 6 18 19 --</td>
<td>2.1</td>
</tr>
<tr>
<td>4.8% Fe/Act.Saran</td>
<td>503</td>
<td>3:1</td>
<td>3.1</td>
<td>-</td>
<td>18 9 12 21 5 18 9 8</td>
<td>1.8</td>
</tr>
<tr>
<td>5.9% Fe/Ox.Saran</td>
<td>503</td>
<td>3:1</td>
<td>3.6</td>
<td>-</td>
<td>20 7 7 17 5 15 10 7</td>
<td>2.0</td>
</tr>
<tr>
<td>5.0% Fe/Carbolac</td>
<td>503</td>
<td>3:1</td>
<td>3.0</td>
<td>-</td>
<td>23 6 11 17 7 17 14 6</td>
<td>1.3</td>
</tr>
</tbody>
</table>

1) Vannice et al. ref.3-6; comparable activity data not available
Figure 4 Weight changes observed in the thermobalance for the 4.4% Fe/RO-0.8 catalyst.
(a) The effect of catalyst pretreatment with hydrogen at 723 K
(b) Synthesis gas conversion over pretreated catalysts at various \( \frac{H_2}{CO} \) ratio's with constant \( p_{CO} \) (0.2 bar) at 673 K
(c) The same as (b) but at constant \( p_{H_2} \) (0.2 bar)

after 20 hours. Deactivation does not stop but slowly continues after that time. (c) The selectivity hardly changes and becomes constant after two hours. This contrasts with results of Fe/SiO\(_2\) and Fe/Al\(_2\)O\(_3\) catalysts, in which case the olefin/paraffin ratio and the methane fraction generally increase as deactivation proceeds.

The high level of CO\(_2\) production shown in Figure 3 is alarming, as it largely exceeds the theoretical maximum amount that balances the CO conversion into hydrocarbons. The excessive CO\(_2\) production must be due to carbon formation by the Boudouard reaction. Its quantity can be calculated from combined carbon and oxygen balances (including a minor correction for the production of water). It turns out that the carbon production exceeds the formation of hydrocarbons roughly by a factor of 2 on C-atom basis, and hence only 20% of the converted CO ends up in hydrocarbons. Remarkably this factor 2 was constant in time and apparently not affected by deactivation. The huge amount of carbon deposition calculated from these data formed the incentive to study these phenomena in more detail by thermobalance experiments and by TEM analysis of used catalysts.

A last point to note is the low level of water production, well below expectations according to the water gas shift reaction. For commercial Fischer Tropsch catalysts and commercial operation conditions equilibrium is usually reached. Feimer et al. [15] and Dry et al. [16] have even shown that most of the CO\(_2\) is formed via water. This is clearly not the case here, probably due to the low \( \frac{H_2}{CO} \)
Figure 5 Typical electron micrographs of carbon deposit after 10 hours of Fischer Tropsch synthesis on a 4.4% Fe/RO-0.8 ($T = 673 \text{ K, } H_2/\text{CO} = 1$).
ratio. As we were curious to know whether the reverse might be true here (H₂O formation via CO₂) we carried out some experiments with CO₂ addition to the feed.

The effect of carbon dioxide addition to the feed

The experiments were carried out by adding CO₂ to the feed gas at constant CO and H₂ partial pressure. This was achieved by replacing part the helium by carbon dioxide. The activity of the catalyst decreased by 60%, while a minor change in selectivity was observed; CH₄ increased (10%), C₂ and C₃ olefins decreased (5%).

The increase in H₂O content was small, indicating that indeed the (reverse) shift reaction is hardly catalysed in our experiments. Remarkably the effect of adding CO₂ is instantaneous and reversible; a switch back to the original feed composition immediately restores the original levels of activity and selectivity.

Thermogravimetric analysis and TEM investigation

The thermobalance experiments were carried out at conditions comparable to the fixed bed experiments described earlier. Weight change versus time plots for the 4.4% Fe/RO-0.8 catalyst are shown in Figure 4, including the effect of catalyst reduction by hydrogen preceding synthesis gas admission. A weight decrease is observed during hydrogen treatment followed by a rapid and large weight increase at synthesis conditions.

In the reduction period an initial rapid weight loss is observed due to reduction of the iron oxide and the simultaneous formation of hydrocarbons known from the fixed bed results (see section on catalyst reduction). After two hours a constant low rate of weight decrease of 2.10⁻⁵ wt% s⁻¹ is seen, corresponding to 0.35 μmol C g⁻¹ iron s⁻¹, and due to continuing methanation of the carrier. At a 8.8% iron loading a proportionally higher rate was found.

The large weight increase observed during synthesis gas conversion is in good quantitative agreement with the calculation made from gas compositions ex fixed bed reactor. Note that a 10% weight increase corresponds to 11.6 C-atoms per Fe-atom, so indeed the quantities are enormous and largely exceed iron carbide formation and surface monolayers.

Figure 4b and c show that increasing the H₂/CO ratio has a significant effect on the carbon deposition rate, although even at H₂/CO = 5 deposition can not be prevented. Increasing the CO partial pressure, either at constant H₂ pressure or at constant H₂/CO ratio enhances the carbon formation, indicating that the reaction order with respect to CO is positive and dominating over the hydrogen influence.

The nature of carbon deposited on the catalyst was revealed by TEM. Pictures of a series of samples with progressive weight increase (Figure 5) show that carbon filaments grow from the catalyst surface with an iron crystallite on top. The filaments have approximately the same diameter as the crystallite. Apparently carbon deposition starts at the interface of the iron crystallites and the carbon
support thus lifting the crystallite from the surface. The fact that carbon deposition remains confined to one side of the crystallite can explain why activity decline is relatively slow and why selectivity patterns are hardly changed: presumably the growing carbon fiber hardly influences the amount of iron surface of a crystallite exposed to gas, while the chemical environment (metal support interaction) does not change either. The observed deactivation is probably due to complete filling or blocking of catalyst pores and not to gradual coverage of the iron surface by (inactive) carbon.

To explain the single-sided growth of carbon one has to assume that carbon atoms formed by CO dissociation on any side of the iron particle can be absorbed by an iron carbide lattice in which they readily diffuse into the existing iron/carbon interface, and crystallize as graphite.

DISCUSSION

Carbon iron catalysts show remarkable properties in synthesis gas conversion, with respect to activity and selectivity. Presumably catalyst preparation and reduction lead to highly dispersed and fully reduced catalysts. Besides the availability of a large surface area an important factor is the presence of reactive carbon which effects direct conversion of iron into a thermodynamically more stable iron carbide phase, having intimate contact with the carbon carrier.

Important features of these iron carbide entities are their immediate activity in Fischer Tropsch synthesis on admission of synthesis gas and their ability to exchange carbon with the support, evidenced by two phenomena. (a) A significant activity of carbon gasification by hydrogen which probably involves hydrogenation of carbon from the iron carbide lattice and replenishment with carbon from the support and (b) the rapidly growing carbon fibers which presumably involve diffusion of single carbon atoms, formed by CO-dissociation, through the carbide phase into the existing carbide/graphite interface.

We think that the key factor responsible for the rapid growth of carbon fibers is the starting situation in which iron has by reaction formed iron carbide in contact with graphite. If one assumes that specific crystal planes of both phases are thermodynamically favoured at the interface, one easily understands continuous growth of graphite at one side of the iron carbide particle.

Obviously this situation is specific for carbon containing carriers and for metal particles that tend to form carbides. Indeed we did not observe a significant weight increase when we studied a Fe-Ru/carbon catalyst, in agreement with the fact that Fe-Ru alloys do not form carbides. (The results of Fe-Ru catalysts, comprising various carriers will be published later).

As to the non-occurrence of the water gas shift reaction and the effect of CO₂ we also think that the stability of the iron carbide is of importance. It is well known that the shift reaction demands the presence of an iron oxide phase [17].
At commercial Fischer Tropsch conditions the high conversion level results in relative high levels of CO$_2$ and H$_2$O which in turn cause partial oxidation of the catalyst into oxide structures. In our case the conversion levels have been confined to a few percent, so the shift catalyst is not formed. The effect of CO$_2$ can be understood from the reversibility of the Boudouart reaction. It is very likely that CO$_2$ is adsorbed dissociatively on iron carbide according to the reaction:

$$\text{CO}_2 + C_{\text{carbide}} \rightarrow 2 \text{CO}_{\text{ads}}$$

Thus CO$_2$ may increase the coverage of iron sites with CO, hinder adsorption and reaction of hydrogen, and consequently reduce the overall activity.

CONCLUSIONS

Iron on carbon catalyst have interesting properties for Fischer Tropsch synthesis, but inherently possess a strong tendency to form graphitic carbon deposits in the form of fibers. The ratio between hydrocarbon synthesis and carbon deposition at CO/H$_2$ = 1 in the feed gas has a constant value of about 2 on C atom basis, irrespective of the extent of deactivation. This indicates that the same active surface area is involved. Deactivation is mainly caused by plugging of catalyst pores. The high initial rate of deactivation is due to the relatively large surface area present in small pores.

As the iron carbide/graphite interaction seems to be the key factor in carbon deposition the problem has to be solved by adding components to iron which avoid carbide formation.

ACKNOWLEDGEMENTS

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