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FORMATION OF OLEFINS FROM SYNTHESIS GAS OVER SILICA-SUPPORTED RuFe BIMETALLIC CATALYSTS

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ABSTRACT
A series of silica-supported Ru/Fe catalysts with different Ru/Fe ratios was investigated. The catalysts were characterized by H2 chemisorption, XRD and TPR/TPO. The activity of the catalysts decreased considerably with increasing Fe content. Maximum olefin selectivity was found at an Ru/Fe ratio of 1:3. The hydrogenation function and the carbon deposition rate of the catalysts are discussed.

INTRODUCTION
Alloy catalysts are of considerable interest in synthesis gas reactions as they may provide a means of improving the selectivity and activity properties. Two active metals in the CO hydrogenation reaction are iron and ruthenium and numerous studies dealing with monometallic catalysts based on these metals have been reported. Only a few studies have dealt with the formation of RuFe alloys.

Ott et al. [1,2] correlated kinetic data with surface compositions of unsupported RuFe catalysts. They observed an increase in olefin selectivity although the catalysts were rapidly deactivated, probably owing to an excessive build-up of carbon. From XPS and SIMS data they concluded that reduced RuFe alloys show considerable iron enrichment in the first atom layer.

Schay and Guczi [3] studied RuFe films deposited under UHV conditions and did not observe any catalytic activity. As no metal oxides were formed, they proposed that oxidic phases are a prerequisite in the formation of active RuFe catalysts. Vannice et al. [4] reported interesting activity and selectivity properties for silica-supported RuFe catalysts. They observed an increase in the olefin to alkane ratio when using alloy compositions with Ru/Fe ratios between 1:2 and 2:1. These results show a close resemblance to those for unsupported RuFe alloys. However, no selectivity enhancement was found for catalysts with a low metal loading (< 1%) [5,7].

This paper reports studies of synthesis gas conversion over silica-supported ruthenium-iron catalysts. The reducibility of the catalysts was studied by TPR experiments. The catalytic properties were examined in a differential fixed-bed reactor and a thermobalance. Olefin hydrogenation experiments were carried out to investigate the affinity of the RuFe catalysts to unsaturated products.
EXPERIMENTAL
Catalyst preparation
The catalysts were prepared by incipient wetness impregnation of the support (AKZO Si-4) with acidified solutions of Fe(NO$_3$)$_3$·9H$_2$O (Merck) and RuCl$_3$·xH$_2$O (Johnson Matthew, 41.83% Ru). The catalysts were dried at 298 K at reduced pressure, followed by thermal treatment at 385 K in air. After this drying period the catalysts were reduced in a flow of hydrogen at 475 K for 2 h followed by passivation in air at room temperature and storage for further use.

Kinetic measurements
The kinetic measurements and the olefin hydrogenation experiments were carried out in a conventional down-flow fixed bed reactor as described previously [8]. Before each experiment fresh catalyst (0.5 g) was reduced in a flow of hydrogen (3 l h$^{-1}$) at 675 K for at least 16 h. After this period the catalyst was cooled to the synthesis temperature, which was usually 550 K. All the experiments were carried out at atmospheric pressure. The gases were obtained from Hoekloos (H$_2$, purity 99.9%; He, purity 99.995%), Matheson (CO, purity 99.5%; C$_3$H$_6$, purity 99.9%) and DSM (C$_2$H$_4$, polymerization grade). The hydrocarbon product distribution (C$_1$-C$_6$) was analysed by GLC.

Temperature-programmed reduction and oxidation
The TPR/TPO apparatus consisted of a microflow reactor, connected to a temperature programmer. At the start of the TPR (TPO) experiment a gas mixture of 5% H$_2$/Ar (5% O$_2$/He) was passed over the catalyst at room temperature. The temperature of the oven was then increased at a linearly programmed rate (5 K min$^{-1}$) and the uptake of hydrogen (oxygen) was measured with a thermal conductivity detector.

H$_2$ chemisorption and X-ray diffraction
The H$_2$ uptake experiments were performed in a conventional glass adsorption equipment. The passivated catalysts were reduced in a flow of hydrogen at 763 K (heating rate 5 K min$^{-1}$) for 2 h, followed by evacuation at 473 K for 1 h. The H/M$^*_t$ values were determined according to the method of Benson and Boudart [9]. The XRD patterns were determined on the passivated catalysts, using a Philips PW 210700 diffractometer.

Thermobalance experiments
These experiments were carried out on a Dupont 950 thermobalance at atmospheric pressure. Experimental details are described elsewhere [8].
RESULTS

Reduction characteristics

In order to characterize the initial state of the RuFe catalysts, TPR experiments on passivated and oxidized catalysts were carried out. The oxidized catalysts resulted from the TPO run with a maximum temperature of 875 K. The TPR profiles of the passivated catalysts are depicted in Figure 1.

Reduction of the 2% Ru/SiO₂ catalyst occurred within the temperature range 350-435 K and was characterized by one peak with a maximum of 380 K. The reduction profiles of the bimetallic catalysts showed the same peak, but it was shifted to higher temperatures with increasing Fe content. Remarkably, the profiles of RuFe (3:1 and 1:3) were characterized by a single peak with maxima at 425 and 435 K, respectively, tailing slightly to higher temperatures. These results contrast with the TPR profiles of room temperature oxygen-treated RuFe catalysts reported earlier by Guczi et al. [10]. They observed two hydrogen uptake peaks at approximately 400 and 670 K.

Only with the RuFe (1:10)/SiO₂ catalyst was more than one H₂ consumption peak observed, indicating a multi-stage reduction process, which is probably due to the reduction of different (surface) metal oxides present on the catalyst carrier.
FIGURE 2  TPR profiles of silica-supported oxidized catalysts: (A) Ru; (B) RuFe (3:1); (C) RuFe (1:3); (D) RuFe (1:10).

viz., oxides of RuFe and Fe. The high temperature range in which reduction occurs (above 500 K) supports the idea that iron oxide is involved, as it is known that high temperatures are required to achieve any H₂ consumption with a supported (pure) iron catalyst. The reduction profiles of both pure Fe and RuFe (1:10) also indicate that, during the TPR experiment, the reduction process of these catalysts is not completed by 875 K.

Reduction of the catalysts treated with oxygen by TPO showed significant differences from the passivated catalysts, as illustrated in Figure 2. With the Ru/SiO₂ catalyst, the maximum hydrogen uptake shifted to higher temperatures (425 K). For the bimetallic catalysts more than one peak occurred in the profile. As the position of the low-temperature peak is in good agreement with the reduction peak of monometallic ruthenium, it is believed that (partial) segregation of metal oxides has occurred. Calculations based on the total H₂ consumption during the TPR experiment indicate that only a small fraction of Ru is present as a separate phase.

Hydrogen chemisorption and X-ray diffraction

To obtain information on the average particle size of the monometallic and bimetallic catalysts, H₂ chemisorption and XRD were applied. With the Ru/SiO₂ catalyst, no line broadening in the XRD pattern was observed, indicating an average particle size of less than 3 nm. H₂ chemisorption resulted in H/M₁ value of 0.34. According to Dalla Betta [11], this value corresponds to an average particle size of 2.5 nm.
TABLE 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ru (wt%)</th>
<th>Fe (wt%)</th>
<th>( \frac{\text{umole metal}}{\text{G}_{\text{catalyst}}} )</th>
<th>H/M_T</th>
<th>Activity (umole s(^{-1}) g(^{-1}) metal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/( \text{SiO}_2 )</td>
<td>2.0</td>
<td>-</td>
<td>198</td>
<td>0.34</td>
<td>174</td>
</tr>
<tr>
<td>RuFe(3:1)/( \text{SiO}_2 )</td>
<td>4.2</td>
<td>0.8</td>
<td>559</td>
<td>0.15</td>
<td>13</td>
</tr>
<tr>
<td>RuFe(1:1)/( \text{SiO}_2 )</td>
<td>3.2</td>
<td>1.8</td>
<td>638</td>
<td>0.12</td>
<td>9.8</td>
</tr>
<tr>
<td>RuFe(1:3)/( \text{SiO}_2 )</td>
<td>1.9</td>
<td>3.1</td>
<td>842</td>
<td>0.09</td>
<td>7.2</td>
</tr>
<tr>
<td>RuFe(1:10)/( \text{SiO}_2 )</td>
<td>0.8</td>
<td>4.2</td>
<td>829</td>
<td>-</td>
<td>4.2</td>
</tr>
<tr>
<td>Fe/( \text{SiO}_2 )</td>
<td>-</td>
<td>5.0</td>
<td>893</td>
<td>-</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Temp. = 550 K, \( \text{H}_2/\text{CO} = 2 \), \( P = 101 \text{ kPa}, W/F = 640 \text{ h}^{-1} \), * after 180 minutes.

For the bimetallic catalysts, the H/M_T value decreased from 0.15 for RuFe (3:1) to 0.09 for RuFe (1:3). Similar observations were made by Kaminski et al. [12] for carbon-supported RuFe catalysts. Based on the calculations of Dalla Betta [11], this should indicate an average particle size of 5-10 nm. However, no line broadening was observed in the XRD pattern.

For the Fe catalysts no significant \( \text{H}_2 \) chemisorption results could be obtained. The line broadening in the XRD spectrum indicated an average particle size of 20 nm.

Activity and selectivity

The rates of the CO hydrogenation, expressed as molar rates per gram of metal for both monometallic and bimetallic catalysts, are shown in Table 1.

The reaction was performed at 550 K, atmospheric pressure and an \( \text{H}_2 \) to CO ratio of 2:1. High space velocities were applied in order to achieve low conversion levels (all below 3%). It appears that the activity of the Ru catalysts is reduced by the introduction of iron, much more than in proportion to their Ru content. The different activity levels are also illustrated in Figure 3, which shows activity-time profiles. The deactivation of the Ru-containing catalysts was strongly depressed relative to the Fe/\( \text{SiO}_2 \) catalyst.

The influence of the Fe content of the bimetallic catalysts on the hydrocarbon product distribution is shown in Figure 4. The hydrocarbon selectivity, expressed in C-atom %, depends strongly on the Ru/Fe ratio. Going from pure Ru to RuFe (1:3) catalyst, a continuous increase in olefin selectivity was observed, the \( \text{CH}_4 \) production showing a complementary decrease.

With the RuFe (1:3)/\( \text{SiO}_2 \) catalyst the ethylene to ethane ratio and the propylene to propane ratios are 3 and 16, respectively, whereas for the Ru/\( \text{SiO}_2 \) catalyst these ratios are close to zero.

Although iron is the most selective single metal for the formation of olefins, its selectivity towards unsaturated products is inferior to those of bimetallic
FIGURE 3 Reaction rates with respect to hydrocarbons as a function of time at 550 K, H₂/CO = 2 and W/F = 640 h. (a) Ru; (b) RuFe (3:1); (c) RuFe (1:3); (d) Fe.

FIGURE 4 Hydrocarbon selectivity corresponding to Figure 3. (●) CH₄, (▲) olefins; (■) alkanes.

catalysts containing 75 mole% of Fe. Monometallic Ru/SiO₂, on the other hand, is far less selective and produces mainly CH₄ (82%), only 5% of the C₂⁺ hydrocarbons being olefins. The selectivity changes are also reflected in the probability of chain growth (α). For Ru, RuFe (1:3) and Fe, α values of 0.33, 0.78 and 0.70, respectively, were found.
Because the CO conversion level can have a relatively large effect on the selectivity pattern, comparative experiments were carried out with the Ru, RuFe (1:3) and Fe catalysts in which the space time was varied. The space time is expressed as W/F, i.e. the catalyst weight (W) divided by the synthesis gas mass flow (F). Figures 5 and 6 show the selectivity and activity data at increasing W/F.

The methane selectivity showed a considerable decrease with increasing space time for iron-containing catalysts. Apparently methane is particularly produced at low W/F, i.e., at a very low conversion level (the highest conversion levels in these series are about 4%). Increasing the W/F value resulted in an increase in CO conversion and a decrease in the hydrocarbon formation rate. Except for Ru, the hydrocarbon product distribution indicated that relatively less CH₄ was formed, a slight increase in C₄ and C₅ products being observed. No significant change in ethylene or propene selectivity was observed.
C$_2$H$_4$ hydrogenation

From the kinetic experiments reported above, it is clear that the olefin selectivity, especially the formation of ethylene, depends strongly on the Ru/Fe ratio. In order to investigate the reactivity of C$_2$H$_4$ in relation to the Ru/Fe ratio, hydrogenation experiments were carried out at an H$_2$ to C$_2$H$_4$ ratio of 3:1 at 550 K.

![Graph showing product distribution of hydrocarbons during the hydrogenation of C$_2$H$_4$ at 550 K before and after (+) the addition of CO (the numbers *3 and *4 are factors by which the indicated concentration values must be multiplied).](image)

For the Ru/SiO$_2$ catalyst (see Figure 7), the experiments clearly show that dissociation of ethylene occurred and methane was formed; CH$_x$ species formed by dissociation also recombined with C$_2$ species, as some propane was also observed. For the RuFe (1:3) catalyst this hydrogenation process was strongly inhibited, whereas for Fe no CH$_4$ or propane was observed. Similar results were obtained in the hydrogenation of C$_3$H$_6$.

When 1 volume % of CO was added to the H$_2$/C$_2$H$_4$ mixture, the conversion of C$_2$H$_4$ was very inhibited. This indicates the preferential adsorption of CO on the catalyst surface, which implies that consecutive reactions involving readsorption of olefins are of little or no importance as long as significant amounts of unreacted CO are present.
FIGURE 8 Weight change versus time plots observed in the thermobalance during reduction and Fischer-Tropsch synthesis at (---) 550 K and (----) 675 K for (a) Fe/SiO$_2$, (b) RuFe (1:3) and (c) Ru/SiO$_2$.

**Thermogravimetric experiments**

As the formation of carbidic structures and other carbon ad-species can also be important to the activity and selectivity properties, we investigated the monometallic Fe and Ru and the RuFe (1:3) catalysts for their tendency to accumulate carbon during the CO hydrogenation. The catalysts were reduced in hydrogen at 675 K until a constant weight was attained. After this period the catalysts were exposed to synthesis gas under conditions comparable to those in the fixed bed experiments described above.

Weight changes versus time plots for these catalysts are shown in Figure 8. The weight increase profiles (broken lines) during the CO + H$_2$ reaction at 550 K show that the rate of carbon formation on the Fe catalyst was lower than that on the bimetallic catalyst. For the monometallic Ru catalysts no significant weight change was observed.

The rate of carbon deposition and the amounts deposited increased strongly for both Fe-containing catalysts as the reaction temperature was increased to 675 K, making them useless at that temperature. The Ru catalyst still behaved well at 675 K.
DISCUSSION

The results indicate that bimetallic RuFe catalysts differ significantly from the monometallic Ru and Fe catalysts or mechanical mixtures of these components with respect to reducibility and activity/selectivity properties [13]. Obviously, this is due to the formation of bimetallic phases.

Evidence for bimetallic phases is that the TPR profiles for the bimetallic catalysts show only a single peak for mixtures containing more than 25 mol% of Ru and that these catalysts are already reduced to a great extent before the reduction of monometallic iron even starts. However, the tailing peak indicates that some heterogeneity exists. Similar observations were made by Niemantsverdriet et al. [14], who studied silica-supported RuFe and RhFe catalysts by Mössbauer spectroscopy. For all these catalysts partial reduction of Fe$^{3+}$ to Fe$^{2+}$ and Fe$^{0}$ was observed at low temperatures. At higher reduction temperatures, signals characteristic of metallic iron ($\alpha$-Fe) were completely absent. Similar features have been reported [15-17] with other bimetallic catalysts consisting of iron and a noble Group VIII metal (PtFe, PdFe).

The low-temperature reduction characteristics can be explained by both thermodynamic and kinetic arguments. Thermodynamically the reduction of iron is eased because the Fe$^{0}$ is stabilized by the alloy structure. Kinetically, Ru atoms may act as catalytic centres at which H$_2$ is dissociated and from which H atoms are transferred to the iron oxide areas of the same particle. However, it is not clear whether the bimetallic particles are fully reduced or not. The contributions of the Fe$^{2+}$ and Fe$^{3+}$ in the Mössbauer spectra have been explained by either a difference in particle size distribution (large, reduced RuFe particles and small, unreduced Fe particles) [14] or by the formation of iron oxidic phases in the bimetallic matrix [18].

The bimetallic particles on the catalyst are irreversible destroyed by the oxygen treatment in the TPR run, i.e., exposure to oxygen pulses up to a temperature of 875 K. This is concluded from a subsequent TPR experiment, which showed a single peak at 380 K, which is characteristic of the reduction of pure Ru oxide. Obviously the oxygen treatment has caused bulk oxidation and partial segregation of the oxide phases. This is in contrast to results reported by Van't Blik [19] for the silica-supported RhFe catalysts. For this system no segregation was observed after a similar oxygen treatment.

The non-linear relationship between activity and composition (Ru content) may be due to several factors. First, particle size might play a role. However, the low H/Mt ratio for the RuFe catalysts does not necessarily imply that larger metal particles have been formed. The adsorption of hydrogen on reduced supported iron catalysts is an activated process [20,21]. Consequently, the H/M values of the bimetallic catalysts give the lower limit of the dispersion. As no XRD line broadening was observed for either Ru or RuFe bimetallic catalysts, we believe that both are well dispersed and have about the
same average particle size. If these ideas are correct, the H/Mₜ data may be seen as a rough measure of the fraction of Ru in the metal surface. The H/Mₜ ratio of 0.15 for the Ru/Fe (3:1) catalyst compared with H/Mₜ = 0.34 for pure Ru may therefore be ascribed to Fe enrichment in the surface of the alloy particles. This effect is to be expected because Fe has a lower surface energy than Ru. This also has been confirmed experimentally \[1\]. H/Mₜ = 0.09 for the Ru/Fe (1:3) catalyst corresponds approximately to 25% of the pure Ru value. This agrees with the fact that below 25 mole% of Fe segregation would take place and a pure Fe phase would be formed, although one should bear in mind that small particles need not follow the "rules" for bulk phases. The difference in catalytic activity between the monometallic Ru and the bimetallic catalysts is therefore believed to be due mainly to the formation of bimetallic particles and to enrichment of Fe at their surface.

Some comments should be made regarding the stability of the bimetallic catalysts and their tendency to form carbon deposits. Deactivation may be caused by several mechanisms. It is well known that iron catalysts rapidly form carbide structures from which graphitic carbon may grow, eventually causing disintegration of the original iron particle. Another form of deactivation involves coverage of the active metal surface by inactive carbon species. Finally, deactivation may be caused by pore blockage due to excessive carbon formation.

The bimetallic catalysts that we studied deactivate at a much lower rate than the pure Fe catalyst. This may correlate with the fact that Mössbauer studies provided evidence that no bulk carbide structures (γ-carbides) are formed during Fischer-Tropsch synthesis when more than 25% mole% of Ru is present, whereas rapid carbide formation takes place with pure iron \[22\].

One might expect that preventing the formation of carbide structures would also prevent carbon deposition. Surprisingly this is not so, as illustrated in Figure 8. The RuFe (1:3) catalysts from carbon deposits in a larger amount and at a higher rate than monometallic Fe. Apparently, part of the bimetallic system is active in the formation of carbon deposits. We believe that these "carbon deposition centres" consist of iron ensembles within the matrix of the bimetallic particle.

The activity of the alloy catalysts with respect to the formation of hydrocarbons is believed to be due to a fraction of the alloy surface in which the active ensembles contain one or more Ru atoms. The presence of Ru atoms in these surface sites will cause a relative increase in hydrogen coverage, which probably prevents carbon deposition on these sites, and hence explains their stability in producing hydrocarbons. In addition, Ru is also known for its activity in dissociating carbon monoxide. Carboneous intermediates (C, CHₓ) might well be formed on Ru and then migrate to the Fe ensembles and become involved in propagation steps. As these Fe atoms are deficient in hydrogen, olefins will be the major product.
Assuming that this hypothesis is correct, the influence of the Ru/Fe ratio on the hydrocarbon product distribution can be understood. Monometallic Ru is an excellent hydrogenation catalyst in many reactions, owing to its ability to adsorb and dissociate hydrogen rapidly, whereas, Fe is a very poor hydrogenation catalyst [23]. Decreasing the Ru content in the alloy catalyst will decrease the availability of hydrogen for the reaction. As olefin formation depends strongly on the hydrogen coverage, it is then expected that the olefin selectivity will increase with increasing Fe/Ru ratio. As it is generally assumed that the synthesis of long-chain hydrocarbons requires larger ensembles of metal atoms, we suggest that the formation of olefins occurs on Fe ensembles that are in intimate contact with one or more Ru atoms.

The experiments in which the space time is substantially changed show that with iron-containing catalysts relatively less methane is produced as the conversion proceeds. This cannot be due to changes in the CO/H\textsubscript{2} ratio as even the higher conversion levels are low (less than 4\%). The only significant changes that do take place in this conversion range are the appearance of CO\textsubscript{2} and H\textsubscript{2}O in the reaction gas mixture. The gases used were extremely pure and dry, and therefore had a high reduction potential, which rapidly declined as small amounts of CO\textsubscript{2} and H\textsubscript{2}O were added by reaction. Our hypothesis, which has not yet been tested, is that the front part of the catalyst bed is kept in a highly reduced state by the feed gas and behaves like an unmodified pure Ru catalyst. Further in the catalyst bed, the amount of surface oxygen, particularly in connection with iron, will increase, leading to the much more selective, partially oxidic Fe or RuFe catalyst. Anyhow, an important warning emerges from these observations: low conversion data for activity and selectivity are non-representative of the performance of these catalysts at practical conversion levels.

Considering the occurrence of consecutive reactions, particularly the conversion of ethylene, no indications were found in these experiments, in agreement with our results on ethylene hydrogenation in the presence of carbon monoxide.

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