Characterization of FeRu/TiO2 and Fe/TiO2 catalysts after reduction and Fischer-Tropsch synthesis by Mossbauer spectroscopy

Citation for published version (APA):

DOI:
10.1016/S0166-9834(00)82925-5

Document status and date:
Published: 01/01/1986

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

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CHARACTERIZATION OF FeRu/TiO₂ AND Fe/TiO₂ CATALYSTS AFTER REDUCTION AND FISCHER-TROPSCH SYNTHESIS BY MöSSBAUER SPECTROSCOPY

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(Received 4 April 1986, accepted 28 May 1986)

ABSTRACT

TiO₂-supported bimetallic catalysts, consisting of iron and ruthenium with metal loading 5 wt.% and molar ratios Fe:Ru = 10:1, 3:1, 1:1 and 1:3 have been investigated with in situ Mössbauer spectroscopy. Ruthenium has a strong influence on the behaviour of the iron in the catalysts. Partial reduction of Fe³⁺ to Fe²⁺ takes place at a lower temperature for FeRu/TiO₂ than for Fe/TiO₂. For reduced Fe/TiO₂ and 10:1 FeRu/TiO₂ catalysts a magnetic sextuplet of α-Fe and bcc-FeRu alloy has been observed and carburization of the iron in these catalysts to x-Fe₅C₂ during Fischer-Tropsch synthesis. The 3:1, 1:1 and 1:3 FeRu/TiO₂ catalysts are only partially reduced to Fe⁰, the latter being present in a hcp-FeRu alloy. With increasing ruthenium concentration and increasing reduction temperature, the initially formed Fe²⁺-phase is transformed back to an Fe³⁺ phase. This Fe³⁺-phase changes partially to an Fe⁶⁺-phase upon chemisorption of CO at 295 K, indicating that the Fe³⁺-phase is highly dispersed. Passivation of the catalysts in air at 295 K results in oxidation of Fe⁰ and Fe²⁺ to Fe³⁺. All passivated FeRu/TiO₂ cata-
lysts show reduction of Fe³⁺ to Fe⁶⁺ by H₂ and by CO at 295 K, which is promoted by the noble metal ruthenium.

INTRODUCTION

Alloying of metals provides a powerful means to optimize the performance of catalysts [1]. Supported bimetallic catalysts of iron and ruthenium have shown interesting selectivities for formation of light olefins, ethylene and propylene in the Fischer-Tropsch synthesis [2]. Recent work by Stoop et al. [3] revealed that FeRu on TiO₂ and SiO₂ with an atomic ratio of Fe:Ru = 3:1 exhibited significantly higher olefin and lower methane selectivities than either of the single metals on TiO₂ or SiO₂ in Fischer-Tropsch synthesis at 575 K and 1 atm.

Mössbauer spectroscopy is an excellent technique to investigate iron-containing catalysts, as the catalysts can be studied in the gaseous environments in which they are active. The purpose of the present study is to compare the chemical state of the iron in a series of FeRu/TiO₂ catalysts with different Fe/Ru ratios as a function of reduction, oxidation, chemisorption of CO and after Fischer-Tropsch synthesis. Mössbauer investigations of FeRu supported on SiO₂ [2,4-7] and of Fe
on TiO₂ [8,9] have been reported in the literature and provide a background for discussion of the results.

Our results indicate that ruthenium has a strong influence on the behaviour of the iron in the catalysts. Below a certain Fe/Ru ratio carburization of the iron in the bimetallic catalysts is not observed during the Fischer-Tropsch synthesis. In addition it is observed that at increasing temperature for reduction in H₂-gas an initially formed Fe²⁺-phase is reoxidized to an Fe³⁺-phase [10]. This unexpected behaviour is more pronounced with increasing ruthenium concentration and is also found for 1:1 FeRu/SiO₂. A systematic study of this behaviour for bimetallic catalysts at different kinds of support is in progress [11].

EXPERIMENTAL

The FeRu/TiO₂ catalysts were prepared by means of pore volume impregnation. An aqueous solution of pH = 1 containing the desired amounts of iron and ruthenium was added dropwise to the TiO₂ support (Degussa, P25, 50 m² g⁻¹) under frequent stirring until the incipient wetness point was reached. As starting materials were used Fe(NO₃)₃·9H₂O (Merck, P.A.), RuCl₃·xH₂O (Johnson Matthey, 41.8% Ru and Fe₂O₃ (90% enriched in ⁵⁷Fe, Oak Ridge). Before dissolving in 2.2 N HNO₃, the Fe₂O₃ had been reduced in flowing H₂. The impregnated catalysts contained a total metal loading of 5 wt%, whereas the iron in the catalysts was enriched in the Mössbauer isotope ⁵⁷Fe. The following samples were prepared: Fe/TiO₂ (4.9% ⁵⁷Fe), 10:1 FeRu/TiO₂ (7.4% ⁵⁷Fe), 3:1 FeRu/TiO₂ (10.9% ⁵⁷Fe), 1:1 FeRu/TiO₂ (10.7% ⁵⁷Fe) and 1:3 FeRu/TiO₂ (14.9% ⁵⁷Fe).

The impregnated samples were dried in air at room temperature for three days, next under vacuum (100 Pa) at room temperature for 24 h and finally in air at 400 K for 24 h. Experiments were carried out on 200 mg of catalyst mixed with 100 mg SiO₂ (Aerosil 300 V), pressed into self-supporting wafers with a diameter of 22 mm using a pressure of 10 MPa. For the investigations of the catalysts at 77 and 4.2 K the wafers were cut to a diameter of 17 mm. The treatments of the catalysts took place in the Mössbauer in situ reactors which have been described elsewhere [12-14]. The gases H₂ (Hoekloos, purity > 99.9%) and CO (Hoekloos, purity > 99.5%) were each purified over a reduced copper catalyst (BASF, R3-11) and a molecular sieve (Union Carbide, SA) at room temperature.

The Mössbauer experiments were done in situ with a constant acceleration spectrometer with a ⁵⁷Co in Rh source. The spectra were not corrected for the varying distance between source and detector, and hence the curved background in the measured spectra is of instrumental origin. Isomer shifts (IS) are reported relative to the NBS standard sodium nitroprusside (SNP) at room temperature. Magnetic fields were calibrated with the 51.5 T field of α-Fe₂O₃ at 295 K. Mössbauer spectra were fitted by computer with calculated subspectra consisting of Lorentzian-shaped lines, by varying the Mössbauer parameters in a nonlinear, iterative minimization routine. In the case of quadrupole doublets the line widths as well as the absorption areas of the two lines were constrained to be equal. A detailed description of this method is given in Ref. [13].
FIGURE 1 Mössbauer spectra of Fe/TiO₂ catalysts after a series of subsequent treatments as indicated measured in situ at room temperature.

RESULTS

Mössbauer spectra at room temperature of the Fe/TiO₂ and FeRu/TiO₂ catalysts after drying, reduction, Fischer-Tropsch synthesis and passivation in air are shown in the Figures 1 and 2. The Mössbauer parameters of the different iron phases contributing to the spectra are listed in Table 1, whereas the decomposition of the spectra into these iron phases is given in Table 2. As the spectra of 3:1 FeRu/TiO₂ and 1:1 FeRu/TiO₂ appeared very similar, we only show those of the former in Figure 2.

Fresh catalysts

The Mössbauer spectra of all fresh catalysts, i.e., the samples after drying in air, consist of a doublet. The spectrum of Fe/TiO₂ contains also a small contribution of a six line component with an average magnetic splitting of about 45.0 T. The values for the Mössbauer parameters of both the doublet and the sextet are characteristic of high-spin Fe³⁺ ions in highly dispersed iron (III) oxide or
FIGURE 2 Mössbauer spectra of 10:1, 3:1 and 1:3 FeRu/TiO₂ catalysts after a series of subsequent treatments as indicated measured in situ at room temperature.

TABLE 1
Average values for Mössbauer parameters of the iron phases observed in the spectra of Figures 1 and 2.

<table>
<thead>
<tr>
<th>Iron phase</th>
<th>IS</th>
<th>QS</th>
<th>ε'</th>
<th>H</th>
<th>Γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe³⁺</td>
<td>0.63±0.02</td>
<td>0.82±0.05</td>
<td>-</td>
<td>-</td>
<td>0.4±0.1</td>
</tr>
<tr>
<td>Fe³⁺ a</td>
<td>0.62±0.02</td>
<td>0.68±0.05</td>
<td>-</td>
<td>-</td>
<td>0.5±0.1</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>1.36±0.03</td>
<td>2.10±0.15</td>
<td>-</td>
<td>-</td>
<td>0.7±0.1</td>
</tr>
<tr>
<td>Fe⁰</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in FeRu alloy</td>
<td>0.26±0.03</td>
<td>0.20±0.04</td>
<td></td>
<td></td>
<td>0.27±0.05</td>
</tr>
<tr>
<td>in α-Fe</td>
<td>0.26±0.02</td>
<td>0.0</td>
<td>331±2</td>
<td>0.33±0.05</td>
<td></td>
</tr>
<tr>
<td>in γ-Fe₅C₃-I</td>
<td>0.45±0.04</td>
<td>0.0</td>
<td>189±2</td>
<td>0.37±0.10</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>0.53±0.04</td>
<td>-0.05</td>
<td>216±2</td>
<td>0.30±0.05</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>0.43±0.06</td>
<td>0</td>
<td>113±5</td>
<td>0.5±0.1</td>
<td></td>
</tr>
</tbody>
</table>

*in bimetallic catalysts after reduction in H₂ at 400 K.
### TABLE 2
Composition (%) of the Mössbauer spectra of Fe/TiO$_2$ and FeRu/TiO$_2$ catalysts after the treatments indicated.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Treatment</th>
<th>$\text{Fe}^{3+}$</th>
<th>$\text{Fe}^{2+}$</th>
<th>hcp-FeRu</th>
<th>$\alpha$-Fe</th>
<th>$\chi$-Fe$_5$C$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/TiO$_2$</td>
<td>fresh</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2$, 400 K, 1 h</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2$, 675 K, 18 h</td>
<td>21</td>
<td>13</td>
<td>66</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>FTS, 575 K, 6 h</td>
<td>3</td>
<td>33</td>
<td>64</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>air, 295 K</td>
<td>28</td>
<td>12</td>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10:1 FeRu/TiO$_2$</td>
<td>fresh</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2$, 400 K, 1 h</td>
<td>3</td>
<td>97</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2$, 675 K, 18 h</td>
<td>4</td>
<td>31</td>
<td>7</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FTS, 575 K, 6 h</td>
<td>4</td>
<td>41</td>
<td>6</td>
<td>6</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>air, 295 K</td>
<td>44</td>
<td>7</td>
<td>7</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>3:1 FeRu/TiO$_2$</td>
<td>fresh</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2$, 400 K, 1 h</td>
<td>5</td>
<td>95</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2$, 675 K, 18 h</td>
<td>27</td>
<td>66</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>FTS, 575 K, 6 h</td>
<td>11</td>
<td>84</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>air, 295 K</td>
<td>90</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:1 FeRu/TiO$_2$</td>
<td>fresh</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2$, 400 K, 1 h</td>
<td>4</td>
<td>96</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2$, 675 K, 18 h</td>
<td>26</td>
<td>68</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>FTS, 575 K, 6 h</td>
<td>13</td>
<td>81</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>air, 295 K</td>
<td>90</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:3 FeRu/TiO$_2$</td>
<td>fresh</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2$, 400 K, 1 h</td>
<td>18</td>
<td>76</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2$, 675 K, 18 h</td>
<td>74</td>
<td>19</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>FTS, 575 K, 6 h</td>
<td>43</td>
<td>47</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>air, 295 K</td>
<td>86</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Oxyhydroxide [15]. Mössbauer spectra of the 1:1 FeRu/TiO$_2$ catalyst at cryogenic temperatures (not shown) showed a doublet at 77 K and partial magnetic splitting at 4 K, with a distribution of hyperfine fields between 40.0 and 50.0 T. This confirms that the iron (III) oxide or oxyhydroxide is present in a highly dispersed state.

**Reduced catalysts**

As the corresponding spectra in Figures 1 and 2 and their analysis in Tables 1 and 2 show, exposure of the catalysts to $\text{H}_2$ at 400 K does not affect the chemical state of iron in monometallic Fe/TiO$_2$, but leads to partial reduction of the $\text{Fe}^{3+}$
in the bimetallic FeRu/TiO$_2$ catalysts. In 10:1, 3:1 and 1:1 FeRu/TiO$_2$ almost all Fe$^{3+}$ present in the fresh catalyst is converted into Fe$^{2+}$ by H$_2$ at 400 K, whereas reduction to Fe$^{2+}$ and Fe$^0$ occurs in 1:3 FeRu/TiO$_2$. The Mössbauer parameters of the ferrous iron, $IS = 1.36 \pm 0.03$ mm s$^{-1}$ and $QS = 2.10 \pm 0.15$ mm s$^{-1}$ are characteristic of high-spin Fe$^{2+}$ in an octahedral coordination [16]. The parameters of the zero-valent iron present in the 1:3 FeRu/TiO$_2$ catalysts, $IS = 0.26 \pm 0.03$ mm s$^{-1}$ and $QS = 0.20 \pm 0.04$ mm s$^{-1}$, correspond to those of Fe$^0$ atoms in hcp-FeRu alloys, as reported by Rush et al. [17].

The final reduction of the catalysts was carried out at 675 K for 18 h. The Mössbauer spectrum of reduced Fe/TiO$_2$ (see Figure 1) is dominated by the six line pattern of $\alpha$-Fe, and contains furthermore small contributions of Fe$^{2+}$ and Fe$^{3+}$. In the reduced 10:1 FeRu/TiO$_2$ catalyst (see Figure 2) the zero valent iron is present as $\alpha$-Fe and as bcc-FeRu alloy, while almost all unreduced iron is present in the ferrous state. The overall degree of reduction of iron is somewhat higher in 10:1 FeRu/TiO$_2$ than in Fe/TiO$_2$. As the recoilless fractions of the different iron compounds in supported catalysts may differ considerably at room temperature [18], degrees of reduction cannot be obtained accurately. Nevertheless, the degree of reduction in our 5 wt% Fe/TiO$_2$ and 10:1 FeRu/TiO$_2$ catalysts is significantly higher than observed with Fe/SiO$_2$ catalysts of comparable loading [19,20].

The Mössbauer spectra of the reduced 3:1, 1:1 and 1:3 FeRu/TiO$_2$ catalysts indicate that iron is present in three different states: Fe$^0$ in hcp-FeRu alloy, Fe$^{2+}$ and Fe$^{3+}$. The contribution of the zero-valent iron to the spectra is only about 6-7%. This is surprisingly small in view of the relatively high degree of reduction in Fe/TiO$_2$ and 10:1 FeRu/TiO$_2$. However, poor reducibility of iron in supported FeRu catalysts has also been reported for FeRu/SiO$_2$ by Guczi et al. and by our group [4-7, 10].

A remarkable result concerning the 3:1, 1:1 and 1:3 FeRu/TiO$_2$ catalysts is that almost all Fe$^{3+}$ in the fresh catalysts can be reduced to Fe$^{2+}$ by H$_2$ at 400 K, whereas after reduction at 675 K a considerable fraction of the iron is in the ferric state. The presence of Fe$^{3+}$ is inferred from the peak in the Mössbauer spectra at 1 mm s$^{-1}$ (see Figure 3a) which is considered as the right-hand part of a doublet with the corresponding counterpart around 0 mm s$^{-1}$. The parameters of this doublet are characteristic for either high-spin Fe$^{3+}$ or low-spin Fe$^{2+}$. Another possibility would be that the peak at 1 mm s$^{-1}$ by itself represents an unresolved doublet of high-spin Fe$^{2+}$, as has been observed in carbon-supported iron catalysts [21,22]. In the latter case a resolved doublet would appear at 77 K [22].

Figure 3a shows the Mössbauer spectra of the reduced 1:1 FeRu/TiO$_2$ catalysts at 295, 77 and 4 K. The 77 K spectrum is similar to the 295 K spectrum and shows in particular that the peak at 1 mm s$^{-1}$ has not split. This excludes the assignment of the 1 mm s$^{-1}$ peak to an unresolved doublet of high-spin Fe$^{2+}$. The 4 K spectrum shows that the doublets of FeRu alloy and Fe$^{2+}$ have not changed, but
that the doublet associated with the 1 mm s$^{-1}$ peak at 295 and 77 K has become magnetically split. This implies that the subspectrum cannot be due to low-spin Fe$^{2+}$ as this state does not possess a magnetic moment. For completeness it is noted that the intermediate spin Fe$^{2+}$ would exhibit magnetic splitting. This state, however, has no known occurrences [16]. Thus, the Mössbauer spectra at 77 and 4 K confirm that the reduced 1:1 FeRu/TiO$_2$ catalyst contains significant amounts of Fe$^{3+}$. The magnetic pattern of this ferric phase accounts for about 40-50% of the area of the 4 K spectrum and is characteristic of a broad distribution in magnetic hyperfine fields. The pattern has no resemblance to the Mössbauer spectra of known iron (III) oxides such as Fe$_2$O$_3$, Fe$_3$O$_4$ or FeOOH.

FIGURE 3 Mössbauer spectra of 1:1 FeRu/TiO$_2$ catalysts measured in situ at 300, 77 and 4.2 K after (a) reduction in H$_2$ at 400 K for 1 h and at 675 K for 18 h subsequently (b) additional Fischer-Tropsch synthesis (H$_2$:CO = 2:1) at 575 K for 6 h.
Catalysts under synthesis gas

The state of iron in Fe/TiO₂ and FeRu/TiO₂ after Fischer-Tropsch synthesis has been investigated by treating the samples in synthesis gas (H₂:CO = 2:1) at 575 K for 6 h, after which a Mössbauer spectrum was recorded at room temperature. The 1:1 FeRu/TiO₂ catalyst after Fischer-Tropsch synthesis was also studied at cryogenic temperatures.

Monometallic Fe/TiO₂ shows carburization of all α-Fe into the carbide χ-Fe₅C₂ [23-25], while simultaneously the residual ferric iron present in the reduced catalyst is converted to Fe²⁺ (see Figure 1, Table 2). Carburization of α-Fe into χ-Fe₅C₂ is also observed for the 10:1 FeRu/TiO₂ catalyst.

When the 3:1, 1:1 and 1:3 FeRu/TiO₂ catalysts are exposed to Fischer-Tropsch synthesis conditions, the major change is that of Fe³⁺, which is abundantly present in the reduced catalysts, into Fe²⁺, whereas the zero-valent iron in hcp-FeRu alloy is not affected by the syngas. Similar behaviour of iron has recently been reported for FeRh/SiO₂ catalysts [18, 26].

Figure 3b shows the spectra of 1:1 FeRu/TiO₂ after Fischer-Tropsch synthesis, measured at 300, 77 and 4.2 K. For the analysis of these spectra, the same arguments apply as for the reduced 1:1 FeRu/TiO₂ catalyst. Comparison of the spectra at 295 K or at 77 K in the Figures 3a and 3b, respectively, indicate that after Fischer-Tropsch synthesis the 1:1 FeRu/TiO₂ catalyst contains less Fe³⁺ than the reduced catalyst. Comparison of the two 4 K spectra reveals that the intensity of the magnetically split pattern in the spectra of 1:1 FeRu/TiO₂ catalyst is less than in that of the reduced catalyst. This confirms once more that the Fe³⁺ doublet at 295 K and 77 K corresponds to the magnetically split pattern at 4 K.

Passivation, rereduction and chemisorption at room temperature

As follows from Figures 1 and 2 and Table 2, upon exposure of the catalysts to air at 295 K after Fischer-Tropsch synthesis, all samples show oxidation of a substantial fraction of Fe²⁺ to Fe³⁺. In all bimetallic FeRu/TiO₂ catalysts investigated here the zero-valent iron in hcp-FeRu alloy is also oxidized by air at room temperature. The carbide χ-Fe₅C₂, as present in Fe/TiO₂ and 10:1 FeRu/TiO₂ appears to be stable in air at 295 K.

Exposure of passivated 10:1, 3:1 and 1:1 FeRu/TiO₂ to H₂ at room temperature leads to a partial reduction of Fe³⁺ to Fe²⁺. This process has been observed in all passivated bimetallic combinations of iron and a more noble group VIII metal [2, 7, 14, 19, 27, 28].

When 3:1 and 1:1 FeRu/TiO₂ catalysts reduced in H₂ at 675 K are exposed to CO at 295 K, reduction of Fe³⁺ to Fe²⁺ occurs, as is shown in Table 3. The same CO-induced conversion of Fe³⁺ to Fe²⁺ has been observed in silica-supported FeRu, FeRh, FeIr and FePt catalysts [6, 7, 27]. The fact that this transition already takes place at room temperature is considered as evidence that the Fe³⁺ ions involved are exposed to the gas phase and, thus, are located at the surface. It
TABLE 3
Composition (%) of the Mössbauer spectra of 1:1 and 3:1 FeRu/TiO₂ catalysts after the treatments indicated

<table>
<thead>
<tr>
<th>Treatment</th>
<th>1:1 FeRu/TiO₂</th>
<th>3:1 FeRu/TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂, 675 K, 1 h</td>
<td>Fe⁰</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Fe³⁺</td>
<td>32</td>
</tr>
<tr>
<td>CO, 295 K</td>
<td>Fe⁰</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Fe³⁺</td>
<td>22</td>
</tr>
</tbody>
</table>

TABLE 4
Composition (%) of the Mössbauer spectra of 1:1 FeRu/TiO₂ catalysts after the treatments indicated

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Fe²⁺</th>
<th>Fe³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>passivated</td>
<td>11</td>
<td>89</td>
</tr>
<tr>
<td>CO, 295 K</td>
<td>83</td>
<td>17</td>
</tr>
<tr>
<td>passivated</td>
<td>8</td>
<td>92</td>
</tr>
<tr>
<td>H₂, 295 K</td>
<td>75</td>
<td>25</td>
</tr>
</tbody>
</table>

is remarkable that the Fe³⁺ species which is formed from the Fe²⁺ phase during the reduction treatment at 675 K in H₂ of the 3:1 and 1:1 FeRu/TiO₂ catalysts (see Figure 2 and Table 2), is partly converted to an Fe²⁺ phase again by the CO-gas at 295 K, as is shown in Table 3.

Also on exposing passivated FeRu/TiO₂ catalysts to CO at 295 K a reduction of Fe³⁺ to Fe²⁺ is observed. For a 1:1 FeRu/TiO₂ catalyst, the reduction by CO at 295 K is compared to the reduction by H₂ at the same temperature in Table 4.

A note of caution concerning such experiments may be appropriate. It is our experience that the degree of reduction of the passivated catalysts for CO as well as H₂ at 295 K, increases with increasing exposure time of CO and H₂. These effects may be due to diffusion limitations in the pressed catalysts wafers. So one has to check by additional measurements on whether or not the exposure time influences the results. All spectra reported here correspond to the final states of the respective reactions.

DISCUSSION

Reduction of FeRu/TiO₂

Reduction of bimetallic FeRu/TiO₂ catalysts in H₂ at 400 K results in partial reduction of almost all Fe³⁺ in the fresh catalysts to Fe²⁺ (see Figure 2). This reduction does not occur in monometallic Fe/TiO₂. Apparently, the presence of Ru in the bimetallic catalysts is responsible for the reduction of iron at relatively
low temperatures. Promotion of the reduction of iron has also been observed in bimetallic FeRh, FePd, FeIr, and FePt catalysts [7] and has been explained in detail for the case of FeRh/SiO$_2$ [28] by a mechanism called "intra-particle hydrogen spillover" [29]. In this explanation noble metal atoms act as nucleation centres where H$_2$ is dissociated into H atoms which diffuse to iron oxide in contact with the noble metal, after which reduction of Fe$^{3+}$ to either Fe$^{2+}$ or Fe$^0$ occurs. Hence the temperature at which the noble metal ions in the fresh catalyst become reduced determines also whether or not Fe$^{3+}$ will be reduced. For example, in freshly prepared FePd/SiO$_2$, Pd reduction starts already below room temperature, as follows from TPR work, and partial reduction of iron at room temperature is observed by means of Møssbauer spectroscopy [30]. Higher temperatures, in the range 550 to 800 K, are necessary for the reduction of monometallic iron catalysts, because the initial step in the reduction process, the reaction between molecular H$_2$ and iron oxide, is more difficult than on noble metal catalysts [28]. The easy reduction of Fe$^{3+}$ to Fe$^{2+}$ in FeRu/TiO$_2$ indicates, therefore, that all iron-containing particles also contain, or are at least in contact with, ruthenium.

The Møssbauer spectra of the Fe/TiO$_2$ and FeRu/TiO$_2$ catalysts after reduction in H$_2$ at 675 K show significant differences. First, the magnetic sextuplets which dominate the spectra of Fe/TiO$_2$ and 10:1 FeRu/TiO$_2$ are virtually absent in the spectra of 3:1, 1:1 and 1:3 FeRu/TiO$_2$. Second, the contribution of zero-valent iron in the spectra of Fe/TiO$_2$ and 10:1 FeRu/TiO$_2$ is high, about 65%, whereas it is less than 10% in the more ruthenium-rich 3:1, 1:1 and 1:3 FeRu/TiO$_2$ catalysts. The magnetic sextet in the spectrum of reduced Fe/TiO$_2$ is characteristic of α-Fe. The magnetic pattern of reduced 10:1 FeRu/TiO$_2$, however, is broadened to the outside. The distribution of hyperfine fields associated with this pattern extends to values which are significantly higher than the 33.0 T field of α-Fe. This part of the distribution is assigned to iron in bcc-FeRu alloy. The occurrence of magnetic fields higher than that of α-Fe is in qualitative agreement with the model of Vincze and Campbell [31] when applied to iron-rich bcc-FeRu alloys with a composition of about 96% Fe and 4% Ru. The FeRu phase diagram [32] indicates that for FeRu alloys with 23% Ru or more the hcp structure prevails, in which magnetic ordering is absent at room temperature. Sextuplets are, therefore, not expected in the spectra of 3:1, 1:1 and 1:3 FeRu/TiO$_2$ catalysts.

The spectra of FeRu/TiO$_2$ after reduction at 400 K demonstrate clearly that Ru enhances the reducibility of iron. Therefore, a remarkable result of this work is that the degree of iron reduction is only below 10% in the Ru-rich 3:1, 1:1 and 1:3 FeRu/TiO$_2$ catalysts, whereas it is high in the Fe-rich Fe/TiO$_2$ and 10:1 FeRu/TiO$_2$ catalysts.

Although a fully reasoned explanation of the phenomena described above has not yet been given, evidence exists that particle size is an important factor. Guzi et al. [33] have found that in FeRu/SiO$_2$ catalysts with metal loadings below 1% reduction of Fe$^{3+}$ to either Fe$^{2+}$ or Fe$^0$ is suppressed, whereas in monometallic
Fe/SiO₂ reduction of Fe³⁺ to Fe²⁺ occurs even at loadings as low as 0.1%. Gučzi [6] has proposed that at low loadings unreduced iron and ruthenium mutually prevent particle growth by impeding migration over the support surface. When applied to the present results, Gučzi's picture suggests that significant particle growth must have been involved in the reduction of Fe/TiO₂ and 10:1 FeRu/TiO₂, but not, or to a lesser extent, in the reduction of 3:1, 1:1 and 1:3 FeRu/TiO₂.

As has first been demonstrated by Garten [34], the extent of iron oxidation after exposing reduced bimetallic catalysts to O₂ at 295 K is a qualitative measure of particle size. By applying this method to the FeRu/TiO₂ catalysts it is observed that iron in Fe/TiO₂ and 10:1 FeRu/TiO₂ does not oxidize very much, whereas in 3:1, 1:1 and 1:3 FeRu/TiO₂ almost all iron is converted into Fe³⁺ by air at 295 K. Thus, the particles in Fe/TiO₂ and 10:1 FeRu/TiO₂, in which a high degree of iron reduction is found, are indeed much larger than those of the 3:1, 1:1 and 1:3 FeRu/TiO₂ catalysts, in which the degree of iron reduction is lower than 10%.

Although Ru enhances the reducibility of iron, it appears that a considerable fraction of the Fe²⁺ present after 400 K reduction has oxidized back to the Fe³⁺ state after the reduction at 675 K. As opposed to what would be expected by intuition, Table 2 shows that the fraction of Fe³⁺ in the reduced catalysts increases with increasing Ru content of the catalysts. Minai et al. [26] observed similar trends for a series of FeRh/SiO₂ catalysts. In their work the fraction of Fe³⁺ in the Mössbauer spectra at 295 K of FeRh/SiO₂ catalysts after reduction at 675 K increased from 51% for a catalyst with Fe/Rh = 1, to 86% for a catalyst with Fe/Rh = 0.03. It should be noted that the presence of large amounts of Fe³⁺ is unequivocally established by spectra of the reduced I:1 FeRu/TiO₂ (see Figure 3a) and I:1 FeRh/SiO₂ [18] at cryogenic temperatures.

A factor which may be involved in the formation of Fe³⁺ during reduction at higher temperatures is segregation of iron to the interface between particle and support. Solid state diffusion will hardly take place at 400 K, but at 675 K it will certainly become significant. In analogy to the well-known phenomenon of chemisorption-induced surface segregation in alloys, it is likely that in supported bimetallic catalysts the component which forms the strongest bonds with the support, iron in the present case, will become enriched at the particle-support interface, where it is stabilized in the Fe³⁺ state. Enrichment of iron at the support will become more important when the bimetallic particles are small, as in the 3:1, 1:1 and 1:3 FeRu/TiO₂ catalysts.

A systematic study of the remarkable formation of ferric from ferrous iron during reduction at temperatures between 400 and 675 K for FeRu catalysts on different supports is in progress [11].
Catalysts under synthesis gas

From the Mössbauer spectra of FeRu/TiO₂ catalysts after Fischer-Tropsch synthesis it follows that in the cases of Fe/TiO₂ and 10:1 FeRu/TiO₂ nearly all the α-Fe and bcc-FeRu alloy in the reduced catalysts is converted into the carbide \( \chi \text{-Fe}_5\text{C}_2 \). The same carbide has been observed in unsupported Fe catalysts [23]. The extent of carburization of the 10:1 FeRu/TiO₂ catalysts is smaller than that of the monometallic Fe/TiO₂ catalysts, which is probably due to a slower carbon diffusion in the bcc-FeRu alloy than in α-Fe.

Carburization during the Fischer-Tropsch synthesis has not been observed in the 3:1, 1:1 and 1:3 FeRu/TiO₂ catalysts. The effect of exposing a reduced FeRu/TiO₂ catalyst to synthesis conditions appears to be similar to the effect of CO at 295 K: Fe\(^{3+}\) is partially converted into a ferrous species while the zero-valent alloyed iron remains unaffected. This behaviour, found before in FeRh/SiO₂ catalysts [18, 26], also occurs in the monometallic Fe/TiO₂ catalysts under synthesis gas and has been attributed to the formation of Fe\(^{2+}\)-CO complexes. Minai et al. [26] reported that the Fe\(^{2+}\) species formed in FeRh/SiO₂ under synthesis gas are not stable towards reduction in H₂ at 675 K, but were converted back to the Fe\(^{3+}\) state. This result in combination with the interpretation given above would imply that the Fe\(^{2+}\)-CO complex on the support is destroyed by H₂, as a result of which the Fe\(^{2+}\) is no longer stabilized and oxidizes back to the Fe\(^{3+}\) state.

Dependent on the Fe/Ru ratio an interesting high activity and selectivity for formation of low olefins has been found for FeRu/TiO₂ catalysts by Stoop et al. [3]. It is interesting that the high selectivity for olefins is found in a compositional region of the bimetallic FeRu/TiO₂ catalysts where neither α-Fe nor bcc-FeRu alloy is observed after reduction at 675 K. In this region the contribution of zero-valent iron in a hcp-FeRu alloy to the spectra is only about 6-7%, whereas the main contributions to the spectra are due to Fe\(^{2+}\) and Fe\(^{3+}\) species. Furthermore no carburization of these catalysts has been observed.

Passivated catalysts

When reduced bimetallic FeM/SiO₂ catalysts are passivated by exposing them to air at room temperature, most of the iron is oxidized to iron (III) oxide. The noble metal M remains in the zero-valent state, except in the least noble bimetallic combination FeRu/SiO₂ in which about half of the ruthenium is oxidized [7]. Oxidation of iron is also observed when FeRu/TiO₂ catalysts used in Fischer-Tropsch synthesis are exposed to air. Only the carbide \( \chi \text{-Fe}_5\text{C}_2 \) appears to be stable in air at 295 K.

The observed partial rereduction of Fe\(^{3+}\) by H₂ at room temperature in passivated 3:1 and 1:1 FeRu/TiO₂ is in agreement with the literature [5, 7, 19, 20, 35, 36]. A remarkable difference in the degree of rereduction by H₂ at 295 K exists between 1:1 FeRu/TiO₂ reported here, and 1:1 FeRu/SiO₂ catalysts [7]. Although
the specific surface areas for the two kinds of supports differ a lot (for SiO$_2$, 310 m$^2$ g$^{-1}$ and for TiO$_2$, 50 m$^2$ g$^{-1}$) the much higher degree of rereduction by H$_2$ for 1:1 FeRu/TiO$_2$ may indicate a stronger stabilization of Fe$^{3+}$ in the case of a SiO$_2$ support. However, an investigation of a bimetallic FeRu/SiO$_2$ catalyst with a specific surface area of the support comparable with TiO$_2$ is necessary for a justified comparison.

When passivated FeRu/TiO$_2$ catalysts are exposed to CO at room temperature, more Fe$^{2+}$ is formed than by exposure to H$_2$, illustrating that CO is a stronger reductor than H$_2$. This effect is even more clear when reduced catalysts are exposed to CO at room temperature. It has been argued before [6,7] that the Fe$^{3+}$ to Fe$^{2+}$ conversion by CO occurs under the influence of the zero-valent noble metal and indicates that the Fe$^{3+}$ ions involved are located at the surface.

Structure of the catalysts

The present Mössbauer results not only yield information on the type of iron species present, but yield also information relating to the structure of the catalyst. For example, a fraction of the Fe$^{3+}$ ions in reduced 3:1, 1:1 and 1:3 FeRu/TiO$_2$ is converted into Fe$^{2+}$ by CO at 295 K. The fact that these ions are accessible for CO at room temperature is regarded as evidence that they form a surface phase. The substantial increase in spectral area of the Fe$^{3+}$ phase between 295 and 4 K in the spectra of 1:1 FeRu/TiO$_2$ (see Figure 3a) is also indicative of surface behaviour [12,18]. Moreover, the fact that this Fe$^{3+}$ to Fe$^{2+}$ transition occurs to a greater extent in air-passivated catalysts, indicates that the ferric surface phase cannot cover the FeRu alloy particles, but forms a separate phase on the TiO$_2$ support. A detailed explanation of this argument has been presented in [6].

Similar conclusions have been drawn on SiO$_2$-supported FeRu, FeRh, FeIr and FePt catalysts [7]. A difference between reduced FeM/SiO$_2$ and the present FeRu/TiO$_2$ catalysts is that the latter contains a significant amount of Fe$^{2+}$, a phase which has not been observed in the SiO$_2$-supported catalysts. The presence of this Fe$^{2+}$ does not permit discussion of the present results in terms of the models proposed for the structure of FeM/SiO$_2$ catalysts [6,7,14,37].

ACKNOWLEDGEMENTS

We thank Mr. E. Gerkema for the skilful assistance with the Mössbauer experiments. J.W.N. acknowledges support from a Huygensfellowship of the Netherlands Organization for the Advancement of Pure Research (ZWO).

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