Characterization of bimetallic FeRh/SiO2 catalysts by temperature programmed reduction, oxidation and Mössbauer spectroscopy

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CHARACTERIZATION OF BIMETALLIC FeRh/SiO₂ CATALYSTS BY TEMPERATURE PROGRAMMED REDUCTION, OXIDATION AND MöSSBAUER SPECTROSCOPY

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ABSTRACT
TPR and Mössbauer experiments on FeRh/SiO₂ catalysts show clear evidence for the formation of bimetallic particles. The degree of reduction in FeRh/SiO₂ is substantially higher than in Fe/SiO₂ catalysts, proving that rhodium acts as a catalyst for the reduction of iron. Oxidation of reduced FeRh/SiO₂ at room temperature mainly causes oxidation of iron while rhodium remains in the metallic state. This is interpreted as being due to the fact that the bimetallic FeRh particles consist of an outer shell enriched in iron, while the core contains most of the rhodium.

INTRODUCTION
It is well known that alloying of two metals can markedly improve catalytic properties such as selectivity and stability, compared to the properties of the constituent monometallic catalysts [1]. From the selectivity point of view, the bimetallic FeRh/SiO₂ catalyst is a very interesting system. Bhasin et al. [2] observed a strong synergistic effect for this catalyst in CO hydrogenation at 300°C and 68 atm. The selectivities to methanol (35%) and ethanol (24%) differed strongly from that of either supported iron or supported rhodium catalysts.

In this paper we present the results of a characterization study of the FeRh/SiO₂ system using temperature programmed reduction and oxidation (TPR and TPO). In situ Mössbauer spectroscopy is applied to obtain information about the chemical state of iron after completion of a TPR or TPO experiment. A more detailed Mössbauer study of the FeRh/SiO₂ system has been published elsewhere [3].

EXPERIMENTAL
Rh/SiO₂ (3.9 wt% rhodium), Fe/SiO₂ (3.5 wt% iron), and FeRh/SiO₂ (5 wt% metal, atomic ratio Fe:Rh = 1:1) were prepared by using the incipient wetness technique. Aqueous solutions of Fe(NO₃)₃.9H₂O (Merck P.A.), RhCl₃.XH₂O (39 wt%, Drijfhout) and a mixture of the two metal salts for the preparation of the bimetallic catalyst were used to impregnate the silica support (Grace, S.D. 2 - 324.382, 290 m² g⁻¹).

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The impregnated samples were dried at room temperature overnight, at 60, 80 and 100°C for 2 h at each temperature, and finally at 120°C for 60 h.

TPR and TPO experiments were carried out with 5% H₂ in Ar and 5% O₂ in He, respectively, with 200 mg catalyst in an apparatus described by Boer et al. [4]. The gases (research grade, Hoekloos) were purified over a BIS column for the removal of oxygen and over molecular sieves (Union Carbide 5A) for the removal of water. The flow rate of gases through the reactor was 5 cm³ min⁻¹ and the temperature was raised at 5°C min⁻¹ within the temperature range of -50 to 500°C. The following sequence of treatments in the TPR apparatus has been used. The sample was heated in Ar at 120°C for 1 h and subsequently cooled to -50°C, after which a TPR profile was recorded. Next, H₂ was removed from the reactor at 500°C by He flushing, to avoid H₂ chemisorption on the catalyst during cooling. After cooling to -50°C in He a TPO profile was measured, followed by cooling to -50°C and flushing with Ar for 1 h. Finally, a second TPR was recorded. The amount of gas consumed during TPR and TPO is expressed per total amount of metal, H₂/M and O₂/M.

As the oxidation states of rhodium and iron before reduction and after oxidation are 3+, the H₂/M value which corresponds to complete reduction of the metals is 1.5. The O₂/M value for complete oxidation of the reduced metal is 0.75.

Chemisorption measurements were performed in a conventional glass system at 25°C. Before measuring the adsorption isotherms the impregnated catalysts were reduced at 500°C (heating rate 5°C min⁻¹) for 1 h under flowing hydrogen and evacuated (10⁻² Pa) at 500°C for another hour. The total amount of chemisorbed H atoms per total amount of metal H/M, was determined according to the method of Benson and Boudart [5].

Mössbauer spectra were measured in situ at room temperature, with 320 mg of FeRh/SiO₂ pressed into a wafer with a diameter of 20 mm. The spectrometer and in situ reactor have been described previously [6]. The spectra were fitted by computer with calculated subspectra consisting of Lorentzian-shaped lines, by varying the Mössbauer parameters in non-linear iterative minimization routine [6].

RESULTS

TPR and TPO profiles of the silica-supported Rh, Fe and FeRh catalysts are shown in Figure 1. The numbers next to the profiles correspond to the ratio between the amount of gas consumed and the total amount of metal in moles.

Reduction of the Rh/SiO₂ catalyst after impregnation and drying occurs within the temperature range of 0-200°C and is characterized by two peaks, one at 95°C, which is assigned to the reduction of Rh₂O₃ (formed during impregnation or drying) and one at 140°C, at which temperature RhCl₃ is reduced [7]. The reduction of the Fe/SiO₂ catalyst is more difficult; it does not start until 200°C. In anticipation of the results of the second TPR, we assign the two peaks to the reduction of Fe(NO₃)₃ (300°C) and Fe₂O₃ (355°C), respectively. The most striking feature of the TPR profile of FeRh/SiO₂ is that reduction takes place mainly within the
FIGURE 1 TPR and TPO profiles of SiO₂-supported rhodium, iron and iron-rhodium catalysts. The numbers next to the curves refer to the total H₂ or O₂ consumption, expressed per total amount of metal atoms in the catalyst. Temperature was increased at a rate of 5°C min⁻¹. Accuracies: H₂/M: ±5%, O₂/M: ±10%.

Temperature range of 0-200°C. This indicates that both metal salts are in intimate contact after impregnation and that rhodium serves as a catalyst for the reduction of Fe(NO₃)₃. The shoulder at 140°C cannot be unambiguously assigned to a compound. The H₂/M values indicate that for the monometallic rhodium catalyst the reduction degree of rhodium is high (95 ±5%), whereas the reduction degree of the iron catalyst does not exceed 42%. This is an upper limit because part of the nitrate may also be reduced, which would contribute to the H₂/M value. Because of this problem, the reduction degrees of the bimetallic FeRh/SiO₂ and the monometallic Fe/SiO₂ catalysts cannot be determined exactly from the H₂/M values.

The TPO profiles (Figure 1) of the reduced catalysts indicate that with all three catalysts oxygen is consumed even at -50°C. The oxidation of the iron catalyst is complete at 300°C, whereas higher temperatures are needed to oxidize the rhodium and the bimetallic catalysts completely. From the observed O₂/M value of 0.75±10% for the bimetallic catalyst, we conclude that the degree of reduction after the thermoduction was high.

Subsequent TPR measurements result in profiles as presented in Figure 1. Rh₂O₃ on SiO₂ is fully reduced below 140°C and the reduction is characterized by a single peak with a maximum at 75°C. Above 150°C the hydrogen consumption is negative, which is caused by desorption of hydrogen from the catalyst surface. Reduction of iron oxide supported on silica occurs above 220°C and at 500°C only
about 30% of the oxide is reduced. The TPR profile of the bimetallic catalyst clearly indicates that after oxidation the two metal oxides are close together, as the reduction is characterized by a single peak at 145°C. The \( \text{H}_2/\text{M} \) ratio for the bimetallic catalyst is 1.43 (±5%), which corresponds to a reduction degree of 95±5%.

The hydrogen chemisorption measurements yielded \( \text{H}/\text{M} \) values of 0.44, 0.01 and 0.16 for the reduced Rh, Fe and FeRh supported catalysts, respectively. These results clearly indicate that the dispersion of the monometallic rhodium catalyst is high. The low \( \text{H}/\text{M} \) value obtained for the monometallic iron catalyst cannot be correlated with dispersion because the degree of reduction of the catalyst is low (about 30%), as confirmed by TPR.

The adsorption of hydrogen on reduced supported iron catalysts is an activated process [8]. Consequently, the \( \text{H}/\text{M} \) value of the bimetallic catalyst gives the lower limit of the dispersion.

To obtain more insight into the oxidation of the iron in the bimetallic catalyst after different stages of reduction and oxidation, Mössbauer spectra were recorded. Figure 2 shows the in situ Mössbauer spectra of the bimetallic catalyst at room temperature after different treatments, as indicated in the figure. The spectra were analysed by applying the appropriate computer program and the Mössbauer parameters are listed in Table 1.

The spectrum of the FeRh/SiO\(_2\) catalyst after reduction at 500°C for 3 h (Figure 2a) consists of a large single line and a shoulder which belongs to a
TABLE 1
Mössbauer parameters of FeRh/SiO₂ at 20°C.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Iron state</th>
<th>IS/mm s⁻¹</th>
<th>QS/mm s⁻¹</th>
<th>LW/mm s⁻¹</th>
<th>Spectral contribution/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh catalyst</td>
<td>Fe³⁺</td>
<td>0.62</td>
<td>0.69</td>
<td>0.44</td>
<td>100</td>
</tr>
<tr>
<td>H₂, 500°C, 3 h</td>
<td>Fe⁰</td>
<td>0.37</td>
<td>-</td>
<td>0.44</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>Fe³⁺</td>
<td>0.61</td>
<td>0.88</td>
<td>0.33</td>
<td>27</td>
</tr>
<tr>
<td>O₂, 20°C</td>
<td>Fe⁰</td>
<td>0.35</td>
<td>-</td>
<td>0.35</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Fe³⁺</td>
<td>0.64</td>
<td>1.03</td>
<td>0.58</td>
<td>82</td>
</tr>
<tr>
<td>O₂, 500°C, 3 h</td>
<td>Fe³⁺</td>
<td>0.64</td>
<td>1.04</td>
<td>0.63</td>
<td>100</td>
</tr>
<tr>
<td>H₂, 500°C, 3 h</td>
<td>Fe⁰</td>
<td>0.35</td>
<td>-</td>
<td>0.47</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>Fe³⁺</td>
<td>0.65</td>
<td>0.87</td>
<td>0.38</td>
<td>25</td>
</tr>
</tbody>
</table>

Accuracies: IS: ±0.03 mm s⁻¹, QS: ±0.05 mm s⁻¹, LW: ±0.10 mm s⁻¹, spectral contribution: ±5%. IS relative to sodium nitroprusside (SNP).

doublet, the left peak of which coincides with the singlet. Evidence that the interpretation in terms of a singlet and a doublet is correct will be presented elsewhere [9]. The isomer shift of the singlet (0.36 mm s⁻¹) is within the range of those for FeRh bulk alloys [10]. Hence, it is assigned to Fe⁰ in the bimetallic crystallite. The Mössbauer parameters of the doublet are characteristic of high spin Fe³⁺ ions. Therefore, we assign the doublet to irreducible iron(III)-oxide in the FeRh/SiO₂ catalyst. The spectral contributions of Fe⁰ and Fe³⁺ are 73% and 27%, respectively (see Table 1). The influence of rhodium on the reduction of iron is obvious because the Mössbauer spectrum of the monometallic Fe/SiO₂ catalyst after 6 h of reduction in H₂ at 500°C showed that the spectral contribution of Fe⁰ was even smaller than 15% [3]. Because of differences in the recoil free fraction of Fe⁰ and Fe³⁺ the degree of reduction of iron in the reduced FeRh/SiO₂ catalyst determined by Mössbauer might be higher than 73%. However, this value will be significantly lower than the value determined by TPR (95±5%). This difference cannot be assigned to diffusion problems in the Mössbauer cell because the spectrum of the reduced FeRh/SiO₂ catalyst did not change on going from a reduction time of 6 h to 70 h. The discrepancy between the reduction degree determined by Mössbauer and TPR is not yet understood.

The spectrum of FeRh/SiO₂ after oxidation at room temperature (Figure 2b) consists for 82% of the spectral area of an Fe³⁺ doublet and for only 18% of the singlet which is due to Fe⁰ in FeRh alloy particles.

Oxidation at 500°C for 2 h leads to a Mössbauer spectrum (Figure 2c) which consists of a Fe³⁺ doublet and consequently only oxidic iron is present. A subsequent thermoreduction at 500°C for 3 h yields a spectrum (Figure 2d) similar to the Mössbauer spectrum obtained after the first reduction.
DISCUSSION

The results of this investigation clearly demonstrate that coclustering of iron and rhodium in the bimetallic FeRh/SiO₂ catalyst occurs since:

(i) FeRh/SiO₂ reduces at lower temperatures than monometallic Fe/SiO₂,
(ii) the degree of reduction in the bimetallic catalyst is substantially higher than in the monometallic iron catalyst, and
(iii) the Mössbauer spectrum of reduced FeRh/SiO₂ indicates that most of the iron is present as Fe⁰ in a FeRh alloy.

Apparently, rhodium, the noble metal, greatly enhances the reducibility of the less noble metal, iron.

Reduction of well dispersed iron on oxidic supports is difficult due to inhibition of the nucleation, i.e. the reaction between molecular H₂ and the metal oxide to produce metal atoms and H₂O [11]. Consequently, the degree of reduction of the Fe/SiO₂ catalysts is low, in our case only about 30%. Supported rhodium catalysts do not suffer from nucleation problems and hence a high degree of reduction up to 100% is observed. The catalytic effect of rhodium in the reduction of the bimetallic FeRh/SiO₂ catalyst can be explained by assuming that the rhodium atoms, reduced by molecular H₂, act as nucleation centres. At these sites H₂ is dissociated to yield H atoms which are sufficiently reactive to reduce oxidic iron. This mechanism is sometimes called "intra particle hydrogen spill over" [12].

The Mössbauer spectrum of reduced FeRh/SiO₂ contains a contribution which we assigned to a doublet of iron(III)oxide. Stronger evidence for this assignment and a more detailed investigation of this oxide will be presented elsewhere [9]. The presence of irreducible material in the catalyst is in accordance with the observed H₂/M value of 1.43, which is lower than the theoretical value of 1.50.

The Mössbauer spectrum of the bimetallic catalyst contains no contributions due to α-Fe or Fe²⁺ phases which are commonly encountered in monometallic Fe/SiO₂ catalysts [3]. Hence, we conclude that isolated iron particles have not been formed. Although the second TPR profiles in Figure 1 indicate that most of the rhodium occurs in a coclustered state with iron, we cannot exclude the presence of some isolated rhodium particles in the bimetallic catalyst, as the TPR curves in repeated runs with oxidized Rh/SiO₂ and FeRh/SiO₂ overlap at temperatures between 60 and 140°C.

Comparison of the TPO profiles for the three catalysts suggests that iron does not promote the oxidation of rhodium in the bimetallic catalyst. The same high temperatures are needed for the complete oxidation of the FeRh/SiO₂ as for the Rh/SiO₂ catalyst. However, the Mössbauer spectrum in Figure 2b shows that oxidation at room temperature converts most of the iron atoms into iron(III)oxide. Only about 20% of the spectrum is due to Fe⁰ atoms in the FeRh alloy. The TPO curve indicates that the degree of oxidation reached at room temperature is of the order of 40%. Combination of these two results leads to the conclusion that oxidation
of the bimetallic FeRh/SiO₂ catalyst at room temperature affects mainly the iron, whereas rhodium remains in a reduced state. An X-ray photoelectron spectroscopy measurement confirmed that rhodium in the passivated FeRh/SiO₂ catalyst is present as Rh⁰ [13].

The results can be understood in the context of a core and shell model for the bimetallic particles. On the assumption that the regular solution model is valid, the two metals are completely miscible, the thermodynamics of this system predicts that the metal with the lowest sublimation energy will be enriched in the surface region of the alloy [14]. As the sublimation energy of iron is lower than that of rhodium, surface enrichment of iron in the reduced FeRh cluster is to be expected. When this bimetallic cluster is exposed to O₂ at room temperature surface enrichment of iron will be even more pronounced. After oxidation at room temperature the particle will consist of an outer shell of mainly iron oxide and a core of FeRh alloy with a high Rh content. High temperatures are necessary for a complete oxidation of the bimetallic cluster. The TPO profile of the FeRh/SiO₂ catalyst above 200°C is similar to that of the monometallic rhodium catalyst and can be assigned to the oxidation of the rhodium core [15].

The TPR profile of the oxidized bimetallic catalyst (Figure 1) is characterized by a single peak and suggests that the oxides are coclustered and that no segregation of the metal oxides has occurred. The temperature at which the reduction takes place is below the temperature above which the oxidized Fe/SiO₂ catalyst starts to reduce and this demonstrates again that clustering of rhodium and iron enhances the reducibility of iron. If rhodium catalyzed the reduction of iron one would expect that reduction of monometallic Rh/SiO₂ and bimetallic FeRh/SiO₂ should start at the same temperature provided that diffusion of H₂ or removal of H₂O is not the rate determining step. However, the reduction of the bimetallic catalyst starts at a significantly higher temperature than that of the monometallic Rh/SiO₂ catalyst. This result is consistent with the proposed core and shell model. As explained before, the formation of the first rhodium metal atoms, the nucleation step, is the rate determining step. In the case of the oxidized bimetallic catalyst the chance of nucleation on the oxide surface is diminished compared to the oxidized monometallic rhodium catalyst, because the rhodium concentration in the outer shell is low due to the surface enrichment of iron.

In order to start nucleation in the core region where the rhodium content is high, hydrogen must diffuse through the outer shell of iron oxide. This process may be rate determining for the reduction and be the cause that the reduction starts at higher temperatures than in systems where rhodium is present at the surface.

Finally, we note that reduction of the bimetallic catalyst after high temperature oxidation leads to the same Mössbauer spectrum as reduction of the impregnated catalyst. Thus, reduction and oxidation of the bimetallic FeRh/SiO₂ catalyst are reversible.
REFERENCES
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