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

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A series of TiO₂-supported bimetallic FeRu catalysts with different Fe:Ru ratios (10:1; 3:1; 1:1; 1:3) has been studied by means of in situ Mössbauer spectroscopy. The influence of reduction and Fischer-Tropsch synthesis on the state of iron in the FeRu/TiO₂ catalysts will be derived.

1. INTRODUCTION

Supported bimetallic catalysts of iron and ruthenium have shown interesting selectivities for formation of light olefins, ethylene and propylene in the Fischer-Tropsch synthesis /1/. Recent work by Stoop et al /2/ 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 investigations of reduced FeRu/SiO₂ catalysts have indicated that iron is present in FeRu alloy and in iron (III) oxide /3-7/. Here we report on the state of iron in FeRu/TiO₂ catalysts during reduction and after Fischer-Tropsch synthesis.

2. EXPERIMENTAL

The catalysts were prepared by impregnating TiO₂ (Degussa, p 25,50 m²/g) with aqueous solution (pH=1) of Fe(NO₃)₃·9H₂O (Merck, p.a) and RuCl₃·xH₂O (Fluca A.G.), until the incipient wetness point was reached. The total metal loading was 5 wt%. Between 5 and 15% of the iron was ⁵⁷Fe. Samples were dried in air at 295 K for 72 h, in vacuum (100 Pa) at 295 K for 24 h and in air at 400 K for 24 h. All further treatments were done in a Mössbauer in situ reactor /8/. Isomer shifts are reported relative to SNP.

3. RESULTS

The Mössbauer spectra of the dried FeRu/TiO₂ catalysts consist of a doublet with IS = 0.63 ± 0.03 mm/s and QS = 0.82 ± 0.05 mm/s, which is characteristic of high-spin Fe³⁺ ions in highly dispersed iron (III) oxide or oxyhydroxide. Figure 1 shows the Mössbauer spectra of the catalysts after intermediate reduction at 400 K, final reduction at 675 K and Fischer-Tropsch synthesis at 575 K (CO/H₂ = ½). As the spectra of 3:1 FeRu/TiO₂ and 1:1 FeRu/TiO₂ are similar, only those of the former are shown. It appears that exposure of the catalysts to H₂ at 400 K does not affect the chemical state of iron in monometallic Fe/TiO₂, but it does lead to partial reduction of the Fe³⁺ in the bimetallic FeRu/TiO₂ catalysts. In 10:1, 3:1 and 1:1 FeRu/TiO₂ almost all Fe³⁺ present in the fresh catalysts is converted to high-spin Fe²⁺ (IS = 1.36 ± 0.03 mm/s, QS = 2.10 ± 0.15 mm/s) by
H₂ at 400 K, whereas reduction to Fe²⁺ and Fe⁰ occurs in 1:3 FeRu/TiO₂. The parameters of Fe⁰, IS = 0.26 ± 0.03 mm/s and QS = 0.20 ± 0.04 mm/s correspond to those of Fe⁰ atoms in hcp-FeRu alloys, as reported by Rush et al. /9/.

After the final reduction of the catalysts at 675 K for 18 h, the Mössbauer spectra of Fe/TiO₂ and 10:1 FeRu/TiO₂ are dominated by a six-line pattern due to α-Fe, and to a combination of α-Fe and bcc-FeRu alloy, respectively. The Mössbauer spectra of the reduced 3:1, 1:1 and 1:3 FeRu/TiO₂ catalysts indicate that iron is present in three different states: zero-valent iron in hcp-FeRu alloy, Fe²⁺ and Fe³⁺. These assignments are confirmed by in situ spectra at 77 K and 4 K as in /10/. The contribution of the zero-valent iron to the spectra, about 6-7%, is surprisingly small in view of the relatively high degree of reduction in Fe/TiO₂ and 10:1 FeRu/TiO₂.

A remarkable result concerning the 3:1, 1:1 and 1:3 FeRu/TiO₂ catalysts is that almost all Fe³⁺ in the fresh catalysts can be reduced to Fe²⁺ by H₂ at 400 K, whereas after reduction at 675 K a considerable fraction of the iron is in the ferric-state. This implies that oxidation of Fe²⁺ to Fe³⁺ has occurred, under H₂, at temperatures between 400 K and 675 K. The oxidation is more pronounced with increasing ruthenium concentration. This unexpected phenomenon is illustrated in more detail in Fig. 2, where spectra of 1:1 FeRu/TiO₂ and Fe/TiO₂ are shown as a function of reduction temperature. As Fig. 2 shows, the degree of reduction in Fe/TiO₂ increases monotonically with increasing reduction temperature. In 1:1 FeRu/TiO₂, however, reduction starts at lower temperatures than in Fe/TiO₂, but when the temperature exceeds 500 K, the doublet due to Fe³⁺ shows a marked increase in intensity. The results show that the Fe³⁺ present in reduced FeRu/TiO₂ catalysts is by no means a residue of Fe³⁺ in the fresh catalysts, and suggest that the ferric
iron reflects the interaction of the FeRu particles with the support.

The Fischer-Tropsch conditions alter the chemical state of the Fe and FeRu/TiO$_2$ catalysts significantly. As shown in Fig. 1 the α-Fe present in reduced Fe/TiO$_2$ and 10:1 FeRu/TiO$_2$ is carburized to x-$\text{Fe}_5\text{C}_2$, and the small amount of Fe$^{3+}$ in these systems is converted to Fe$^{2+}$, as also observed on exposing 3:1, 1:1 and 1:3 FeRu/TiO$_2$ catalysts to Fischer-Tropsch synthesis. The zero-valent iron in hcp-FeRu alloy, however, is not affected by syngas. Similar behaviour of iron has been reported for FeRh/SiO$_2$ catalysts /10,11/.

4. DISCUSSION

The fact that partial reduction of iron in H$_2$ at 400 K occurs in all FeRu/TiO$_2$ catalysts and not in Fe/TiO$_2$ demonstrates that Ru enhances the reducibility of iron, similarly as in SiO$_2$- and Al$_2$O$_3$- supported FeRu catalysts /5/. Several investigations before /4,12,13/ have shown that in supported bimetallic catalysts consisting of iron and a noble group VIII metal promotion of the reduction of iron by the noble metal takes place. As explained before /14/, the noble metal provides the sites where H$_2$ is dissociated into H atoms which diffuse to contiguous iron oxide, where Fe$^{3+}$ is reduced to Fe$^{2+}$ or Fe$^0$. Thus, the results indicate that all iron containing particles in the fresh catalysts contain or are in contact with ruthenium.

In spite of the presence of ruthenium and its reduction-promoting abilities, reduction of 3:1, 1:1 and 1:3 FeRu/TiO$_2$ catalysts at 675 K does not lead to formation of substantial amounts of zero-valent iron as in the Fe/TiO$_2$ and 10:1 FeRu/TiO$_2$ catalysts. The extent to which iron in FeRu/TiO$_2$ catalysts is reduced at 675 K, even decreases with increasing Ru content. Minai et al /11/ observed similar trends for a series of FeRh/SiO$_2$ catalysts, while Berry et al /5/, on the other hand, found the opposite for Al$_2$O$_3$-supported
FeRu catalysts. We suggest that the formation of Fe$^{3+}$ by back oxidation of Fe$^{2+}$ during reduction at more elevated temperatures, shifts to lower temperatures by increasing ruthenium content. In analogy with chemisorption-induced surface segregation in alloys it seems likely that the formation of Fe$^{3+}$ during reduction is associated with segregation of iron in the FeRu particles to the support, where it is stabilized as Fe$^{3+}$. A systematic investigation of the reduction behaviour of FeRu on different supports is presently in progress.

Mössbauer spectra of the catalysts after Fischer-Tropsch synthesis show that carburization occurs only in Fe/TiO$_2$ and iron-rich 10:1 FeRu/TiO$_2$. Nearly all zero-valent iron present in $\alpha$-Fe and bcc-FeRu alloy is converted into $\chi$-Fe$_5$C$_2$, which carbide is also the main component in unsupported Fe catalysts after Fischer-Tropsch synthesis /15/. The catalyst with the highest olefin selectivity is 3:1 FeRu/TiO$_2$ /2/. It is interesting to note that this catalyst contains iron predominantly as Fe$^{2+}$ and Fe$^{3+}$, that the contribution of Fe$^{0}$ in hcp-FeRu to the Mössbauer spectrum at 295 K is only about 6% and that carburization of this Fe$^{0}$ does not occur.

References