

On the Properties of Silica-Supported Bimetallic Fe–Cu Catalysts

Part I. Preparation and Characterization

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In this work a series of silica-supported bimetallic iron–copper catalysts has been prepared and characterized. The bimetallic catalysts were prepared via homogeneous deposition–precipitation involving a procedure in which first copper ions (as copper hydrosilicate) and consecutively iron(III) ions (as goethite) are precipitated onto the support. The results show that copper facilitates the reduction of iron(III) to iron(II) (which is present as iron(II)silicate) as well as the reduction to zero-valent iron. In the reduced iron/copper catalyst zero-valent iron is present as monometallic α -Fe particles and as iron clusters in bimetallic Fe–Cu particles. The relative amounts of the various iron species vary with the overall composition. Whereas the surfaces of the freshly reduced bimetallic particles are not extensively enriched in one of the constituents, prolonged CO exposure at room temperature leads to a considerable iron enrichment. © 1990 Academic Press, Inc.

INTRODUCTION

The conversion of syngas (CO/H₂) to hydrocarbons via the Fischer–Tropsch synthesis is a well-known process (1–3). A variety of catalysts, all containing as the most important component one of the Group VIII metals (such as Ru, Co and Fe), is used in this reaction. Their activity, selectivity, and deactivation patterns have been widely studied. Especially iron-based catalysts usually yield a product mixture consisting mainly of *n*-paraffins, *n*-olefins, and (at elevated pressures) *n*-alcohols. A large number of publications and patents have been published dealing with methods and procedures to increase the selectivity of the iron catalysts to low-molecular-weight olefins (4, 5) and oxygenated products (6). In

addition to the rather poor selectivity, deactivation of the catalyst in the Fischer–Tropsch reaction is another important problem. Loss of activity can be due to fouling, poisoning, sintering, and extensive carbon deposition (1). With transition metal catalysts the deposited carbon species can exhibit a variety of properties and morphologies (7, 8). For instance, with iron catalysts at high CO/H₂ ratios and elevated temperatures, growth of carbon whiskers can occur (1). As a result the structure of the catalyst completely disintegrates and in a fixed-bed reactor plugging occurs.

Geus and co-workers (9, 10) have presented evidence that in the temperature range 650–1000 K filament growth on iron catalysts occurs via a decomposing iron carbide phase. As copper is inactive in carbide formation it was anticipated that dilution of the iron atoms by alloying with copper atoms may be an effective procedure to suppress the formation of iron carbides and

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thus whisker growth. However, it has been established that the formation of (surface) iron carbides is a prerequisite for iron catalysts to exhibit the desired activity in the Fischer-Tropsch reaction (1-3, 11, 12). Thus, alloying iron catalysts with inactive copper may also lead to changes in the selectivity and activity.

Detailed knowledge of the structure and composition of bimetallic catalysts is necessary in order to properly evaluate their catalytic performance. Therefore, in this work we report on the preparation and characterization of such bimetallic catalysts and in a subsequent paper we will deal with the catalytic performance of these catalysts in the Fischer-Tropsch synthesis.

The bimetallic catalysts were prepared by homogeneous-deposition precipitation via a procedure in which the metal precursors were consecutively applied onto the support. Temperature-programmed reduction (TPR) experiments were carried out to characterize the precipitates in more detail and to study the effect of copper on the reduction behavior of iron. Mössbauer spectroscopy was used to identify the various iron species in the reduced catalysts and to establish the degree of iron reduction. Transmission electron microscopy was used to assess the metal particle size and the distribution of the metal particles over the support. Infrared spectra of adsorbed carbon monoxide were used to investigate (in a qualitative way) the surface composition of the bimetallic iron/copper catalysts.

EXPERIMENTAL

Catalyst Preparation

The Fe-Cu catalysts were prepared by consecutive deposition of copper and iron atoms onto the silica support (Degussa, aerosil 200 m²/g). First, copper ions were precipitated from an aqueous copper nitrate solution onto the bare support by homogeneously raising the pH of this solution via urea decomposition at 353 K. In the cop-

per/silica catalyst thus obtained the copper ions are present in a copper hydrosilicate phase (13). The copper/silica catalyst was filtered off from the solution and redispersed in demineralized water. Next, an acidified (pH 1) iron(III)nitrate solution was slowly injected (0.2 nmol/liter) at 353 K into this suspension, the pH of which was kept constant (pH 6) by a pH-stat, which controlled by means of a peristaltic pump the supply of a 0.1 M NH₄OH solution. In previous work it was shown that under these conditions iron(III) ions are exclusively deposited as small goethite (α -FeOOH) particles onto the silica support (14). After completion of the filtration the bimetallic catalyst was filtered off from the solution, washed with demineralized water, and air-dried overnight at 393 K. Catalysts were prepared with 20% wt total iron plus copper loading and with atomic compositions covering the entire compositional range. Catalysts are denoted by the atomic composition Fe(at.%)Cu(at.%).

Characterization

TPR experiments were carried out with fresh samples (dried for 16 h in a 2% vol O₂/He stream at 393 K) in an apparatus described by Kock *et al.* (15). Typically, a quantity of 10 mg was reduced in a 10% vol H₂/Ar mixture at a flow rate of 0.80 ml/s (heating rate 0.16 K/s). In the electron microscopic investigations (Philips EM 420) passivated samples were used. Passivation was carried out by exposing the reduced and flushed catalysts at room temperature to still air. The infrared spectroscopic experiments were performed using the transmission-absorption technique. Wafers (25 mg) were pressed at 80 MPa and mounted into the vacuum apparatus. Details of the transmission experiments and the vacuum system have been given in a previous publication (16). After dosing 13.3-kPa CO to the reduced catalysts, spectra were recorded at room temperature with a Perkin-Elmer 580B spectrophotometer connected to a 3500-CDS data station. Fresh samples

were reduced in a flow of 10% vol H_2/Ar at 773 K (after raising the temperature stepwise at 100 K per h) for 16 h followed by outgassing at 673 K; the lower evacuation temperature was used to prevent oxidation by desorbing water molecules. Mössbauer spectra were recorded with a constant acceleration source using a ^{57}Co in Rh source. Isomer shifts are reported with respect to the NBS standard sodium nitroprusside. Literature isomer shifts, calibrated versus α -Fe, have been recalculated and refer to the nitroprusside standard in this paper. Magnetic hyperfine fields were calibrated with the 515 kOe field of α - Fe_2O_3 at room temperature. The spectra were not corrected for the varying distance between the source and the detector, and hence the curved background in the measured spectra is of instrumental origin. The Mössbauer parameters were determined by fitting the spectra with reference subspectra consisting of Lorentzian-shape lines using a non-linear iterative minimization procedure (17). In the case of quadrupole doublets the line widths as well as the absorption areas were constrained to be equal. The Mössbauer spectra were collected at 300, 77, and 4.2 K using a reactor permitting the *in situ* measurement of spectra under any desired gas atmosphere. All reported spectra were measured in a hydrogen atmosphere. The hydrogen/argon mixture used in all experiments was of technical quality (Hoekloos). The gas mixture was deoxygenated by passing either through a copper catalyst (BASF R-3-11) or through a Pd/ Al_2O_3 catalyst. Subsequently, the gas mixture was dehydrated by passing it through a column containing a molecular sieve (Linde 4A). In the infrared experiments ultrapure carbon monoxide (AGA gas 99.997% vol) was used without further purification.

RESULTS

TPR profiles of the freshly prepared silica-supported Fe, Cu, and Fe–Cu catalysts are shown in Fig. 1. For comparison the reduction behavior of a physical mixture of

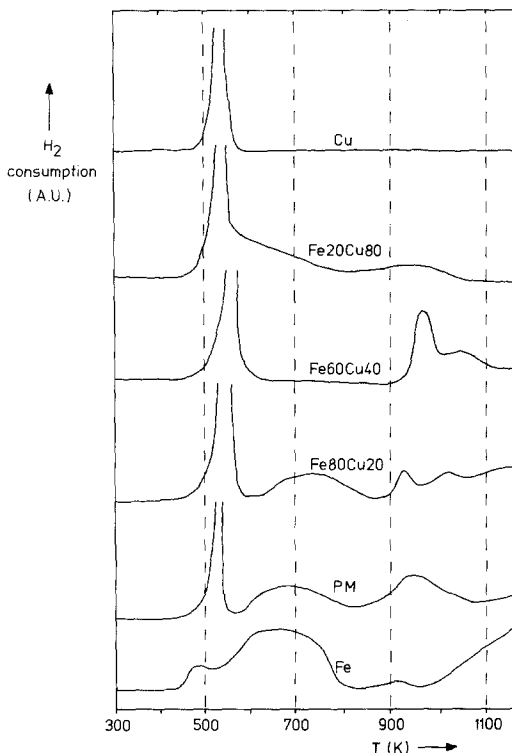


FIG. 1. TPR profiles of the freshly prepared iron-copper catalysts. PM is physical mixture (Fe/Cu = 50/50 at./at.).

the pure copper/silica and iron/silica catalysts has also been studied (atomic Fe/Cu ratio in the physical mixture is unity). The reduction profile of the copper/silica catalyst is characterized by one sharp peak at about 540 K due to the reduction of the copper hydrosilicate phase (13). With the iron/silica catalyst, reduction proceeds in two steps, viz., a broad peak between 500 and 800 K and a peak above 900 K. The broad low-temperature peak is due to the reduction of α - $FeOOH$ (goethite) to iron(II) silicate (14), which is partly reduced to metallic iron above 900 K. Whereas in the temperature range between 500 and 800 K the reduction of the bimetallic samples virtually proceeds in one step (except for the iron-rich Fe–Cu catalyst), the physical mixture reduces in two separate steps. In fact, the reduction profile of the physical mixture

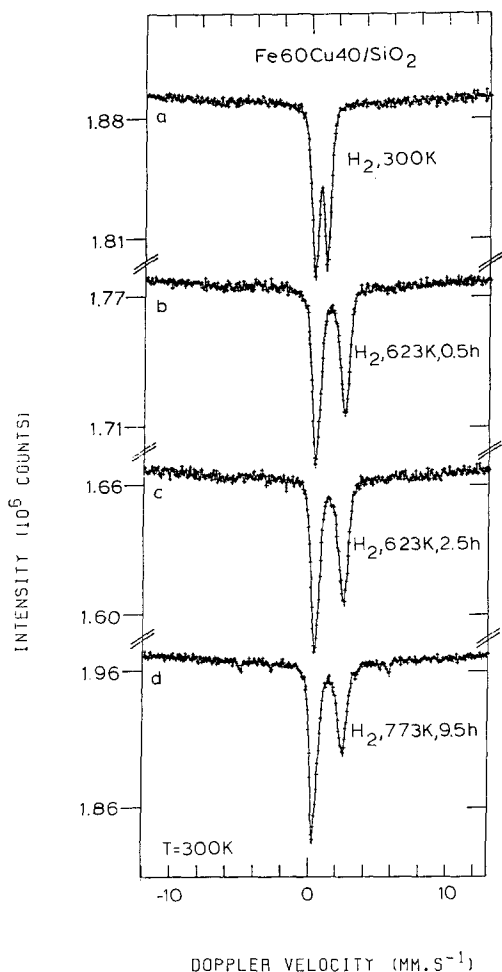


FIG. 2. Room-temperature Mössbauer spectra recorded with the Fe60Cu40 catalyst reduced under progressively more severe conditions.

is a superposition of the reduction profiles of the pure iron/silica and copper/silica catalysts. It can thus be concluded that in the Fe-Cu catalysts (especially with the copper-rich bimetallic catalysts) copper facilitates the reduction of the iron(III) precursor, indicating that both the iron- and copper precursors are deposited in intimate contact onto the support. Above 900 K the TPR profiles of the physical mixture and the bimetallic catalysts show a small hydrogen consumption peak, which is due to the reduction of the iron(II)silicate compound (*vide infra*). The onset temperature of the

reduction of this compound is not strongly affected by the presence of copper.

In Figure 2 Mössbauer spectra are shown of a Fe-Cu catalyst (containing 60 at.% Fe) reduced under progressively more severe conditions. The Mössbauer parameters that can be deduced from these spectra are listed in Table 1. The spectrum of the fresh bimetallic iron/copper catalyst consists of a doublet with parameters characteristic of a high-spin Fe^{3+} compound, such as $\alpha\text{-FeOOH}$ (16). The Mössbauer spectrum recorded after reduction at 623 K for 0.5 h shows that the Fe(III) species is reduced to an iron(II) compound. The asymmetric doublet present in this spectrum has been deconvoluted to a doublet and a singlet. The Mössbauer parameters of the doublet are characteristic for an iron(II)silicate phase (14) and the singlet indicates the presence of zero-valent iron atoms, which are (on the basis of the $\text{IS} = 0.17 \text{ mm/s}$) most probably present as small iron clusters in a copper matrix (18-23). The spectrum recorded upon subsequent reduction under more severe conditions (773 K, 9.5 h) shows the formation of $\alpha\text{-Fe}$.

With regard to the deconvolution procedure we note that a fit which describes the doublet with two (or more) symmetric doublets instead of one symmetric doublet may be more appropriate since in the iron(II)sili-

TABLE 1

Mössbauer Parameters^a of Fe60Cu40 Catalyst Reduced under Progressively More Severe Conditions

Pretreatment	Iron state	IS (mm/s)	QS (mm/s)	H (kOe)	% area
Fresh	Fe^{3+}	0.73	0.89		100
623 K/0.5 h	Fe^{2+}	1.42	2.01		86
	Fe^0	0.17			14
623 K/2.0 h	Fe^{2+}	1.40	1.99		88
	Fe^0	0.18			12
773 K/9.5 h	Fe^{2+}	1.40	1.93		70
	Fe^0	0.17			24
	Fe^0	0.32		324	6
773 K/16	See Table 2				

^a Accuracies: IS, $\pm 0.03 \text{ mm/s}$; QS, $\pm 0.05 \text{ mm/s}$; spectral contribution, $\pm 5\%$.

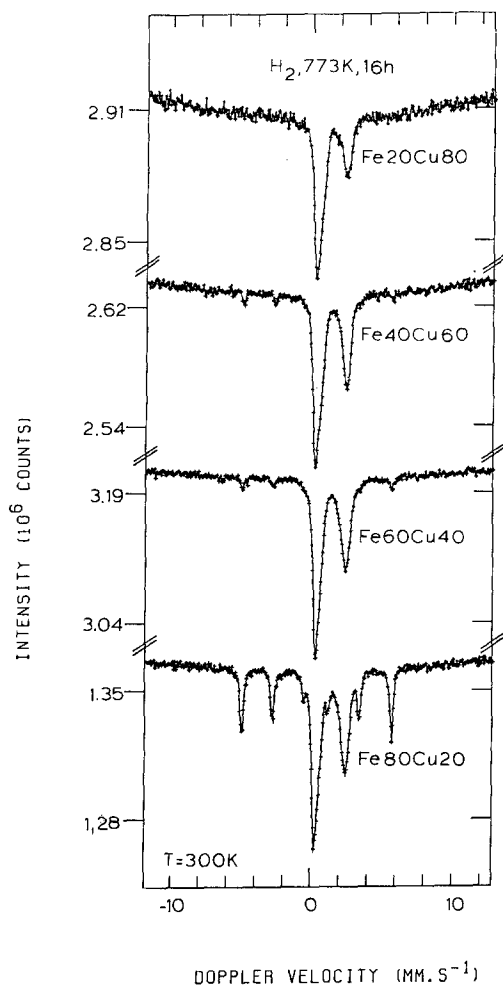


FIG. 3. Room-temperature Mössbauer spectra of different iron-copper catalysts collected after reduction at 773 K for 16 h.

cate compound the Fe^{2+} ions are present in different environments and as a consequence this compound is characterized by an asymmetric doublet (24, 25). However, in doing so the relative resonance areas of the species involved are not markedly affected.

In agreement with the results of the TPR experiments, the Mössbauer spectra show that (under similar experimental conditions) with the iron/copper catalysts a considerably higher degree of iron reduction can be attained than that with a pure iron catalyst (14). The effect of copper on the

degree of reduction and on the relative amounts of the various iron species present in the reduced bimetallic catalysts can be appreciated from the Mössbauer spectra shown in Fig. 3 and from the data given in Table 2. It appears that at high copper concentrations the amount of $\alpha\text{-Fe}$ is virtually nil and only zero-valent iron atoms are present, characterized by a singlet with IS varying from 0.12 to 0.20 mm/s.

In order to further characterize the zero-valent iron species giving rise to the singlet, Mössbauer spectra of the reduced Fe20Cu80 catalyst were measured at 77 and 4.2 K (Fig. 4). Unfortunately, due to the presence of the iron(II)silicate compound the spectrum at 4.2 K is significantly broadened, making a straightforward interpretation complicated. Nevertheless, a comparison of the present low-temperature Mössbauer spectra with spectra previously reported for a pure iron(II) silicate compound (14) shows the predominant presence of the central line in the bimetallic iron/copper catalyst. Furthermore, the spectrum recorded at 4.2 K with the bimetallic iron/copper catalyst shows a small

TABLE 2

Mössbauer Parameters^a of Different Fe-Cu Catalysts after Standard Reduction Treatment (773 K for 16 h)

Catalyst	Iron state	IS (mm/s)	QS (mm/s)	H (kOe)	% area
Fe20Cu80	Fe^{2+}	1.45	1.75		52
	Fe^0	0.20			48
Fe40Cu60	Fe^{2+}	1.41	1.90		66
	Fe^0	0.12			28
Fe60Cu40	Fe^0	0.31		330	5
	Fe^{2+}	1.40	1.93		70
	Fe^0	0.17			24
Fe80Cu20	Fe^0	0.30		318	6
	Fe^{2+}	1.38	1.95		54
	Fe^0	0.15			14
Fe100 ^b	Fe^0	0.30		331	32
	Fe^{2+}	1.33	2.26		39
	Fe^{2+} ^c	1.29	1.66		39
	Fe^0	0.29		329	22

^a Accuracies are given in Table 1.

^b Reduced at 823 K for 6 h.

^c Iron(II)silicate doublet fitted with two symmetric doublets (see text).

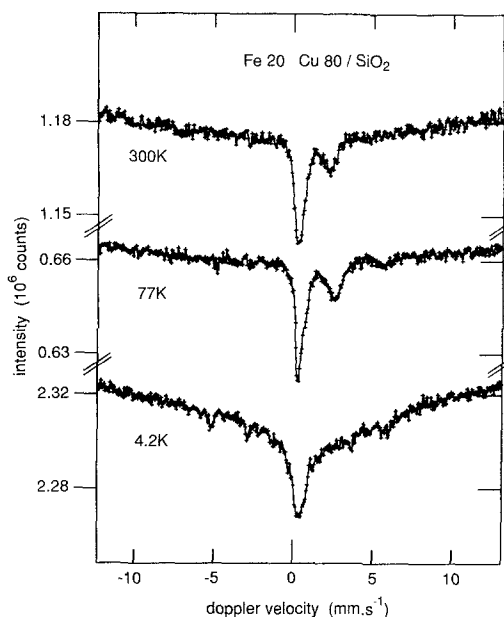


FIG. 4. Mössbauer spectra recorded at different temperatures of reduced (773 K, 16 h) Fe₂₀Cu₈₀ catalyst.

contribution with a magnetic hyperfine splitting.

Whereas Mössbauer spectroscopy monitors mainly the bulk composition of the bimetallic catalyst, information on the surface composition of the reduced iron/copper catalyst can be obtained from the infrared spectra of adsorbed CO. To that end the freshly reduced and evacuated samples were exposed at room temperature to 13.3 kPa carbon monoxide. The spectra recorded after a 3-min exposure to CO are shown in Fig. 5. Independent of the composition four bands are present in the spectra, viz., a band at 2170 cm^{-1} , a broad band with a maximum between 2125 and 2105 cm^{-1} , a broad band between 1960 and 1925 cm^{-1} , and a small band at 2010 cm^{-1} . Following earlier assignments (14, 26) it seems fair to assign the band at 2125–2105 cm^{-1} to the vibration of a CO molecule linearly bonded on a copper atom. The band at 1960–1925 cm^{-1} and the band at 2010 cm^{-1} are characteristic for linearly bonded CO molecules on zero-valent iron atoms. Whereas the po-

sition of the peak maximum of the 1960–1925 cm^{-1} band varies with the overall composition, the band at 2010 cm^{-1} appears to be independent of the bulk composition. Since also the position of the CO–Cu bands varies with the overall composition, it can be argued that the iron atoms characterized by the lower frequency band (1960–1925 cm^{-1}) are present together with the reduced copper atoms in a bimetallic entity, whereas the iron atoms giving rise to the high-frequency band (2120 cm^{-1}) are located in monometallic iron particles. The lower frequency of the CO–Fe band of the iron atoms present in the bimetallic particles is accounted for by dilution effects (27). The 2170 cm^{-1} band is due to CO adsorbed on iron(II)silicate (14).

Upon prolonged CO exposure marked changes in the spectra are observed. As a

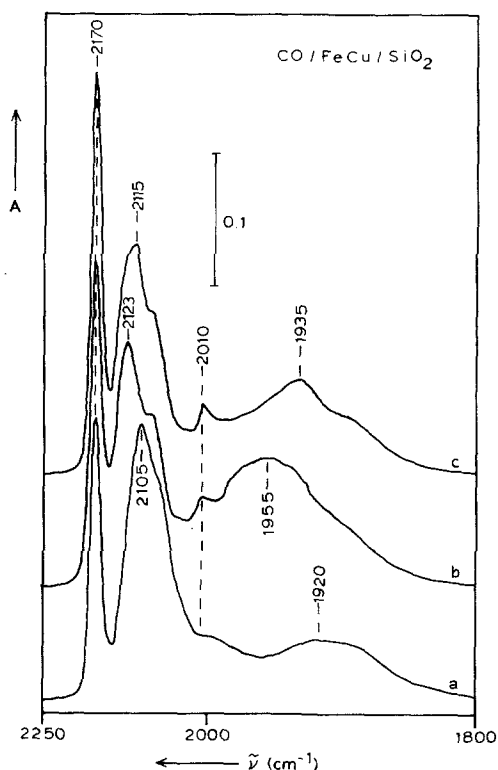


FIG. 5. Infrared spectra of adsorbed CO (13.3 kPa) on reduced iron-copper catalysts. (a) Fe₂₀Cu₈₀; (b) Fe₆₀Cu₄₀; (c) Fe₈₀Cu₂₀.

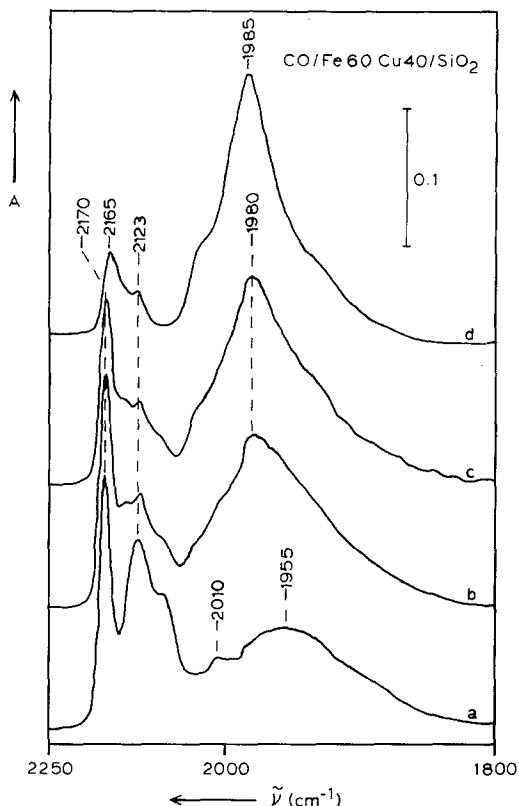


FIG. 6. Infrared spectra illustrating the effect of prolonged CO exposure (13.3 kPa at room temperature) to Fe₆₀Cu₄₀. Spectra recorded after exposure for (a) 5 min; (b) 2 h; (c) 4 h; (d) 24 h.

typical example the results are shown in Fig. 6 for the reduced Fe₆₀Cu₄₀ catalyst. With increasing CO exposure the following features are evident. (i) The intensity of the band around 1955 cm⁻¹ (CO-Fe) increases at the expense of the intensity of the band around 2123 cm⁻¹ (CO-Cu). Furthermore, the peak maximum of the former band continuously shifts to a higher wavenumber. (ii) The intensity of the 2170-cm⁻¹ band also decreases (but much more slowly than the CO-Cu band) and simultaneously the intensity of the band at 2010 cm⁻¹ (present as a shoulder on the broad peak centered around 1980 cm⁻¹) increases. Whereas the intensity changes described in (i) appear to be typical for the bimetallic Fe-Cu particles, the intensity changes given in (ii) are

characteristic for a partly reduced Fe/SiO₂ catalyst (14).

In Fig. 7 two representative electron micrographs are shown of the reduced (773 K, 16 h) and statically passivated Fe-Cu catalysts. These micrographs show that the mean metal particle size is about 10–20 nm in the iron-rich bimetallic catalyst and 15–30 nm in the copper-rich catalyst, showing that the mean metal particle size slightly increases with the copper concentration.

DISCUSSION

The TPR profiles indicate that reduction of the copper hydrosilicate and reduction of the iron ions from the ferric to the ferrous state proceed in one step with the Fe-Cu catalysts containing more than 40 at.% Cu. With the physical mixture and the iron-rich Fe-Cu catalyst these processes occur in two consecutive steps. Apparently, in the copper-rich bimetallic Fe-Cu catalysts copper serves as a catalyst for the reduction of Fe(III) to Fe(II) provided the copper and iron precursors are in close proximity. The catalytic effect of copper can be explained by assuming that at elevated temperatures hydrogen adsorption and dissociation occur on the reduced copper atoms. Provided the two metal precursors are in close contact the hydrogen atoms can migrate to the Fe(III) species which are then reduced to Fe(II). It has been reported that with bimetallic iron catalysts containing a noble metal (Pt, Pd, Rh, or Ir) as the other constituent, reduction of Fe(III) to Fe(II) (and sometimes even to Fe(0)) can occur in a hydrogen atmosphere even at room temperature (28, 29).

Precipitation of copper at 353 K onto a silica support leads to the formation of copper hydrosilicate which is homogeneously distributed over the support (13). On the basis of the structure of the copper hydrosilicate (30) and the specific surface area of the silica support, one can calculate that about 10% wt Cu ions is required for the formation of a monolayer of this compound on the silica particles. Since Fe(III) ions are

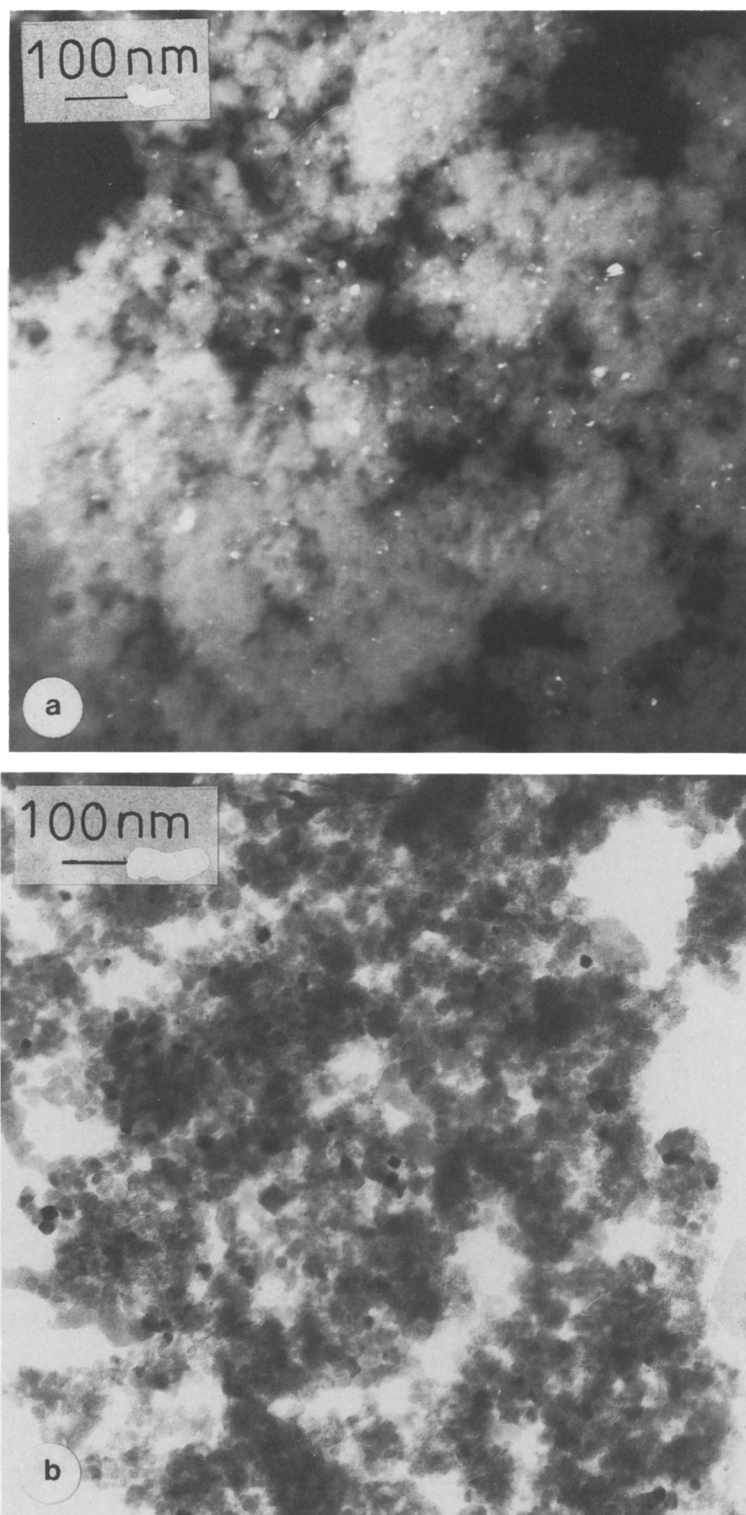


FIG. 7. Typical electron micrographs of two passivated (after reduction at 773 K for 16 h) iron-copper catalysts. (a) Dark field micrograph of Fe₈₀Cu₂₀; (b) bright field micrograph of Fe₂₀Cu₈₀.

subsequently precipitated onto this material as α -FeOOH, it can be envisaged that provided the copper loading is equal to or higher than 10% wt Cu (that is, in our case about 44 at.% Cu) the two metal precursors must be in close contact. This is supported by the TPR results showing that the catalytic effect of copper on the reduction of Fe(III) to Fe(II) is most clearly expressed with the copper-rich bimetallic catalysts.

The Mössbauer spectra show that copper not only catalyses the reduction of Fe(III) to Fe(II) but also facilitates the reduction to zero-valent iron atoms, which are either present in α -Fe particles (especially in the iron-rich catalysts) or as small iron clusters in a copper matrix (especially in the copper-rich catalysts) giving rise to a singlet with an IS between 0.12 and 0.20 mm/s. This latter attribution calls for a brief discussion. Using Mössbauer spectroscopy various authors have studied the Fe–Cu system (18–23) and the results of these studies indicate that various different iron species can be present in this bimetallic system. (i) The first are isolated iron atoms in solution giving rise to a singlet with an IS of approximately 0.46 mm/s (23). (ii) Secondly, there are clusters of iron atoms characterized by a doublet with an IS shift which decreases from about 0.46 to 0.14 mm/s depending on the amount of iron atoms present in the cluster. It has been reported that for each iron atom added to the cluster the IS decreases stepwise with 0.02–0.03 mm/s (23). (iii) Eventually in such a cluster the central iron atom is surrounded by 12 iron atoms as nearest neighbours and as a consequence the cluster behaves as γ -Fe characterized by IS = 0.14 mm/s. (iv) Although an IS = 0.14 mm/s has been reported to be characteristic for γ -Fe, Keune *et al.* (18) have shown that in copper-rich Fe–Cu films iron clusters different from γ -Fe but nevertheless exhibiting at room temperature the same isomer shift are present.

Since γ -Fe exhibits small antiferromagnetic splitting the broadening of the central line in the 4.2-K spectrum recorded with

the reduced Fe₂₀Cu₈₀ catalyst indicates that the iron clusters in our bimetallic catalyst are indeed γ -Fe. However, the low-temperature spectrum also shows (albeit to a very small extent) a contribution pointing to the presence of iron clusters with properties similar to those found by Keune *et al.* (18). Most probably, both types of iron clusters are present in our reduced Fe–Cu catalysts. Since both types of iron atoms exhibit Mössbauer parameters characteristic of iron clusters in a copper matrix, we conclude that in the reduced Fe–Cu catalyst bimetallic particles are present containing both copper atoms and iron atoms (in the form of small clusters). However, besides these bimetallic particles, in particular the iron-rich Fe–Cu catalysts, contain monometallic α -Fe particles. This interpretation is supported by the results of infrared experiments.

The four bands present in the infrared spectra of adsorbed CO with the reduced Fe–Cu catalysts arise from CO adsorption on iron(II)silicate (2170 cm⁻¹), iron atoms in reduced monometallic iron particles (2010 cm⁻¹), and iron (around 1940 cm⁻¹) and copper atoms (around 2110 cm⁻¹) present in bimetallic Fe–Cu particles. This latter attribution is supported not only by the fact that the peak position of these two bands varies with the overall bulk composition but also by the changes observed upon prolonged CO exposure, indicating that the amount of iron atoms in the surface of the bimetallic particle slowly increases at the expense of the copper atoms. In fact, eventually copper has virtually disappeared from the surface, indicating that the surfaces of the bimetallic particles are strongly enriched in iron. Iron enrichment is also indicated by the continuous shift of the CO–Fe band from 1955 to 1985 cm⁻¹ with increasing intensity (that is, with increasing amount of adsorbed CO on iron atoms) which can be explained by an increasing dipole–dipole interaction between the vibrating CO molecules (27). We note that CO-induced iron segregation is to be expected

from the appreciable differences in the heats of CO adsorption on the respective metals: $\Delta H(\text{CO}-\text{Cu}) = -63 \text{ kJ/mole}$ and $\Delta H(\text{CO}-\text{Fe}) = -167 \text{ kJ/mole}$ (31-33). Thus, the infrared experiments support the presence of true bimetallic particles containing both copper and iron atoms in the reduced Fe-Cu catalysts.

The infrared data also provide evidence for the presence of monometallic iron particles in the reduced Fe-Cu catalysts. This is not only evident from the presence of the 2010-cm^{-1} band but also from the changing intensity of the 2170- and 2010-cm^{-1} bands upon prolonged CO exposure, which was reported to be typical for a partly reduced Fe/SiO₂ catalyst (14). Briefly, these results indicate that the reduced monometallic $\alpha\text{-Fe}$ particles are initially partly encapsulated by a silica overlayer. However, it has been argued that upon prolonged CO exposure the shape of the iron particles changes, leading to an increased amount of reduced iron surface atoms, thus accounting for the intensity increase of the 2010-cm^{-1} band and the concomitant intensity decrease of the 2170-cm^{-1} band.

Thus, both the infrared and the Mössbauer experiments suggest the presence of monometallic iron particles and bimetallic iron-copper particles in the reduced Fe-Cu catalysts. In addition to the two types of metal particles a significant amount of unreduced iron(II)silicate is also present.

As can be seen from the results given in Table 2, the relative amount of the various species present in the reduced catalysts varies with the overall composition. In order to offer an explanation for this observation we will briefly discuss the factors influencing the genesis of the various species. The Mössbauer results show that copper not only catalyses the reduction of ferric ions to ferrous ions, but that it also facilitates the reduction to zero-valent iron atoms present in the bimetallic particle. With the monometallic iron/silica catalyst it has been shown that reduction at 623 K leads to the exclusive formation of

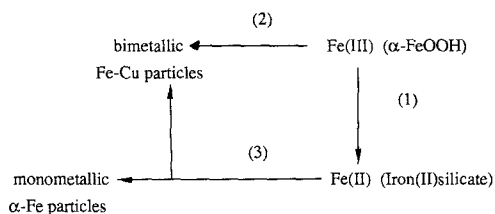


FIG. 8. Schematic of the processes occurring during the reduction of the bimetallic iron-copper catalysts.

iron(II)silicate (14). Our present results show that at this temperature with the bimetallic catalysts reduction to zero-valent iron already proceeds, suggesting that with increasing copper concentration the amount of ferrous ions which reacts to iron(II) silicate decreases and that concomitantly the amount which can be directly reduced to zero-valent iron (present in the bimetallic particle) increases. However, with increasing iron concentration a greater amount of ferrous ions reacts with the silica to iron(II) silicate. Reduction of this iron(II) silicate compound proceeds at a more elevated temperature, leading not only to zero-valent iron present in the bimetallic particles, but also to the formation of monometallic $\alpha\text{-Fe}$ particles. Schematically, the process occurring during the reduction of the Fe-Cu catalysts are given in Fig. 8. The presence of copper influences both pathway 1 and pathway 2: at high copper concentrations pathway 2 is favoured over pathway 1. Route 3 is not markedly influenced by the presence of copper (TPR results).

CONCLUSIONS

The following conclusions can be drawn from this work.

(i) Mössbauer spectra show that reduction of the bimetallic iron-copper catalyst leads to the formation of iron(II) silicate and zero-valent iron, which is present as monometallic $\alpha\text{-Fe}$ particles and as iron clusters in a copper matrix forming bimetallic Fe-Cu entities. The relative amounts of these three iron species strongly depend on the overall composition.

(ii) In the bimetallic Fe–Cu catalysts copper facilitates the reduction of the ferric to ferrous ions and the partial reduction to zero-valent iron. Hydrogen migration from the reduced copper atoms to the ferric ions is thought to be responsible for the enhanced reducibility of the ferric ions. Most probably, reduction to zero-valent iron is facilitated since the reduced iron atoms can be stabilized in the copper matrix.

(iii) Whereas the surfaces of the freshly reduced alloy particles are not extensively enriched in one of the constituents, prolonged CO exposure at room temperature leads to a considerable enrichment of iron in the surfaces of the bimetallic particles.

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