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Effect of Rhodium Traces on the Reducibility of Silica-Supported Iron Particles

Eric Bonnefille · Jean-Marc M. Millet ·
Jean-Pierre Candy · Jean Thivolle-Cazat ·
Ronan Bellabarba · Robert Tooze · Jean-Marie Basset

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Abstract Fe/SiO_2 and $Rh–Fe/SiO_2$ catalysts with increasing Fe/Rh ratio have been prepared and characterized by TEM, XRD, oxygen adsorption and Mössbauer spectroscopy. It was confirmed that Fe/SiO_2 catalysts cannot be reduced under hydrogen flow, to more than 50 % whatever the temperature in the 200–500 °C range and shown that the presence of even a small amount of Rh (Fe/Rh $\leq$2,000) promoted the reduction of iron up to 85–95 %. This promoting effect also took place with a $Fe/SiO_2 + Rh/SiO_2$ physical mixture (Fe/Rh $\leq$2,000). Therefore, the occurrence of a hydrogen spillover effect may be involved in the observed process.

Keywords Rhodium · Iron · Reducibility · Promoting effect · Mössbauer · Oxygen absorption

1 Introduction

Iron was formerly the basic metal used as supported catalyst in Fischer–Tropsch synthesis, transforming the syngas ($CO + 2H_2$) into a mixture of hydrocarbons [1]. Later, it was found that $Rh–Fe/SiO_2$ catalysts could produce an appreciable amount of oxygenate products ($\geq$50 %), i.e. mainly methanol and ethanol besides methane [2–9]. This type of catalyst also showed interesting properties in selective hydrogenation of α-β-unsaturated aldehydes [10, 11]. The preparation of such catalysts generally involved the classical incipient wetness method for impregnation of silica or other supports, from an aqueous mixture of salts of both metals in similar or various proportions; [2, 12] sometimes, the deposition of mixed Fe–Rh clusters was used for that purpose [13–15]. Various characterization studies have also been performed on $Fe–Rh/SiO_2$ or Fe–Rh/C systems showing the formation of alloys under reductive conditions as well as a promoting effect of rhodium on the reducibility of iron; [12, 16] the promoting effect on iron reduction was also observed with other $Fe–M/SiO_2$ [17, 18], Fe–M/C [19, 20] (M = Co, Ni, Ru, Rh, Pd, Ir and Pt) or $Fe–Pd/Al_2O_3$ [21] bimetallic systems involving a noble metal where the reducing agent was mainly hydrogen and sometimes CO; [21] however in every case, even after a treatment under flowing hydrogen at high temperature (400–500 °C) the

E. Bonnefille · J.-P. Candy · J. Thivolle-Cazat (✉)
ICL, C2P2 UMR 5265 (CNRS-CPE-Université Lyon 1)
LCOMS-CPE-Lyon, Université de Lyon, 43 Boulevard du 11 Novembre 1918, 69616 Villeurbanne, France
e-mail: thivolle@cpe.fr

E. Bonnefille
e-mail: eric.bonnefille@free.fr

J.-P. Candy
e-mail: candy@cpe.fr

J.-M. M. Millet
Institut de Recherches sur la Catalyse et l'Environnement de Lyon IRCELYON, UMR5256 CNRS-Université de Lyon, 2 Avenue A. Einstein, 69626 Villeurbanne, France
e-mail: jean-marc.millet@ircelyon.univ-lyon1.fr

R. Bellabarba · R. Tooze
Sasol Technology (UK) Ltd, Purdie Building, North Haugh, St Andrews, Fife KY16 9ST, UK
e-mail: ronan.bellabarba@eu.sasol.com

R. Tooze
e-mail: bob.tooze@eu.sasol.com

Present Address:
J.-M. Basset
KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology, Thuwal, Kingdom of Saudi Arabia
e-mail: jeanmarie.basset@kaust.edu.sa

reduction of iron in these bimetallic systems proved incomplete [19].

Similarly, Batley et al. [22] showed the influence of small amounts of Pt atoms on Co reduction. This result was later confirmed by Holmen and coworkers [23] and more recently, Bianchi [24] showed that not only Pt, but other transition metals such as Ru, Ir could promote the reduction of Co. Nevertheless, it is necessary to note that all the samples supported on alumina, reduced under the experimental conditions of these studies, never showed a complete Co reduction to the metal species even at 900 °C. Conversely, Goodman and co-workers [25] showed that silica-supported Co catalyst, doped by small amount of Rh (0.1 % Rh, 15 % Co) were fully reduced at 400 °C.

In this paper we report on the effect of very small amounts of Rh in Fe–Rh/SiO_2 catalysts on the reduction extent of iron by hydrogen. For that purpose, Fe–Rh/SiO_2 catalysts treated at different temperatures under hydrogen and getting various reduction degrees have been characterized by Mössbauer spectroscopy of ^{57}Fe and volumetric measurement of oxygen uptake.

2 Experimental

2.1 Catalysts Preparation

2.1.1 *Synthesis of Fe/SiO_2 from an Aqueous Solution of $FeCl_3$*

The silica support was an Aerosil 200 from Degussa with a specific surface area of 200 m^2/g. In a typical preparation, a solution of iron (III) chloride $FeCl_3$ (1.452 g, 5 wt% Fe equiv. introduced) in 25 ml of permuted water was progressively added at pH 4, to a well-stirred aqueous suspension of silica (10 g; 50 ml) in a jacketed reactor maintained at 25 °C. A solution of sodium hydroxide (0.2 M, 15 ml) was added when required, via a servo-syringe controlled by a pH-meter (Hanna Instruments (pH 500–212) with a double junction Tuff Tip gelled pH electrode provided by Bioblock^{TM}), to neutralize the formation of H_3O^+ [26]. At the end of $FeCl_3$ addition, the suspension was stirred during 4 h. After filtration, the solid was dried under vacuum (10^{-3} mbar) at increasing temperature up to 100 °C and stored in air.

Natural iron contains only 2.2 % of the ^{57}Fe isotope active for gamma-nuclear resonance (Mössbauer) absorption; so that, with natural iron loading of 1.62 and 3.57 wt%, the ^{57}Fe amount in the catalysts was considered too low to record Mössbauer spectra in the better conditions. Therefore, a ^{57}Fe enriched precursor ($^{57}FeCl_3$ with 98 % ^{57}Fe) was used for the preparation of a ^{57}Fe/SiO_2 sample dedicated to the Mössbauer characterization. 30 mg (0.526 mM) of ^{57}Fe enriched turning, purchased to Eurisotop, was dissolved in 3 ml of concentrated HCl (Aldrich) to form a solution of $^{57}FeCl_3$. ^{57}Fe was then deposited onto 500 mg of silica with the same procedure as that used for unlabelled Fe, to obtain a ^{57}Fe loading of 5.33 wt% (5.44 wt% total Fe).

2.1.2 *Synthesis of Rh–Fe/SiO_2 and Rh–^{57}Fe/SiO_2 Bimetallic Catalysts*

One gram of Fe/SiO_2 solid was treated under hydrogen during 4 h at 400 °C. After cooling, the catalyst was covered with 20 ml of pure deoxygenated water (pH 7). An aqueous solution of $[RhCl(NH_3)_5Cl_2]$ (11.5 mg, 0.4 wt% Rh introduced) went through an ion exchange resin (Amberlite IRN 78) and dropped onto the Fe/SiO_2 solid in aqueous suspension. The suspension was stirred during 4 h. After filtration, the solid was dried at increasing temperature up to 100 °C under vacuum and stored in air. The Rh–^{57}Fe/SiO_2 bimetallic catalyst was prepared in the same way, starting with 500 mg of ^{57}Fe/SiO_2.

2.1.3 *Preparation of a Fe/SiO_2 + Rh/SiO_2 Physical Mixture*

The Fe/SiO_2 + Rh/SiO_2 physical mixture was prepared by mixing 1.06 g of the 3.57 wt% Fe/SiO_2 catalyst with 11 mg of a 0.31 wt% Rh/SiO_2 sample previously reduced under H_2 at 500 °C; the whole was manually grinded in an agate mortar. This catalyst was thus previously reduced at 500 °C under flowing H_2 (10 ml/min) before O_2 uptake measurements as for the other Fe–Rh catalysts.

2.2 Catalysts Characterization

2.2.1 *Oxygen Uptake on Fe/SiO_2 or Rh–Fe/SiO_2 Catalysts*

Oxygen uptake on Fe and Rh–Fe catalysts was measured using a home made static volumetric apparatus previously described [27]. The catalyst (500 mg) was introduced into a cell connected to the volumetric apparatus and treated under a hydrogen flow (10 ml/min) at the required temperature for 10 h. After cooling the reduced solid to room temperature, the event of the cell was sealed under hydrogen; the solid was further desorbed under vacuum at 300 °C (2 h up to 300 °C and 2 h at 300 °C). After cooling again at 25 °C, oxygen was introduced into the cell, the sample was heated at 400 °C for 4 h and the pressure value noted when back at room temperature. Assuming that after this later treatment, Fe and Rh are both in the fully oxidized state (Fe^{III} and Rh^{III}) [28], the oxygen uptake was deduced from pressure variation, and used to determine the total reduction degree of the sample.

The pressure gauge of the apparatus is a Barocell 655 AB 1,000 mbar from Edwards. Its resolution is better than 0.1 mbar and the whole volume of the working cell is close to 100 cm^3, so that, the experimental error from the amount of oxygen uptake on a 500 mg sample is less than 0.002 mmol/g. Blank experiments done with the silica support alone have shown that adsorption of oxygen is close to 0.001 mmol/g under 100 mbar, so that it can be neglected. The iron and rhodium weight content of the samples were determined at the "Service Central d'Analyse, USR-59/CNRS, Solaize, France". The experimental error of these analyses is estimated as less than 5 %.

2.2.2 *Electron Microscopy and X-ray Diffraction*

Transmission electron microscopy (TEM) was carried out using a JEOL 100 CX electron microscope. TPR coupled with X-ray diffraction powder patterns were recorded using a Panalytical X'Pert Pro MPD diffractometer equipped with an Anton Paar XRK 900 reactor chamber (Cu Kα radiation, X'Celerator detector with 127 channels used). Data were collected in continuous scanning mode at 0.016552°/s, i.e. 2 s per step of 0.033° (2θ) and 256 s per data point. The sample was heated at various temperatures from 25 to 500 °C under flowing H_2 (40 ml/min). The X-ray patterns were recorded every fifty degrees after a 30 min dwell time.

2.2.3 *Mössbauer Spectroscopy*

The Mössbauer spectrometer is a home made apparatus described elsewhere [29]. The Rh–Fe/SiO$_2$ powder was treated in a glass reactor fitted with a side arm bearing the Mössbauer cell so that the catalyst can be transferred without any contact with air. Spectra of the powder samples were recorded using a 2 GBq ^{57}Co/Rh source and a conventional constant acceleration spectrometer, operated in triangular mode. The isomer shifts (δ) were given with respect to α-Fe. The relative areas of observed spectral components have been used to quantitatively evaluate the relative amounts of the iron species present in the catalysts. This has been done by assuming equal recoil-free fractions for all Fe species.

3 Results and Discussion

3.1 Fe/SiO$_2$ Catalysts

Two Fe/SiO$_2$ catalysts with Fe contents of 1.62 and 3.57 wt% and another one of 5.44 wt% Fe with 98 % ^{57}Fe content, were prepared and characterized (see "Experimental" section).

Electron Microscopy of the 3.57 wt% Fe/SiO$_2$ sample shows that during the preparation treatments, rather large iron particles of size ranging between 15 and 25 nm are formed (Fig. 1).

In order to determine the effect of temperature on the iron reduction degree, a quantitative titration by oxygen adsorption was performed using the 1.62 wt% Fe/SiO$_2$ sample (see "Experimental" section). Curiously, the reoxidation of the reduced Fe/SiO$_2$ required a prolonged heating at 400 °C (around 4 h) under partial pressure of oxygen before reaching a stabilized pressure value. A total reduction degree of the Fe/SiO$_2$ samples was determined by comparing the amounts of oxygen uptake for each

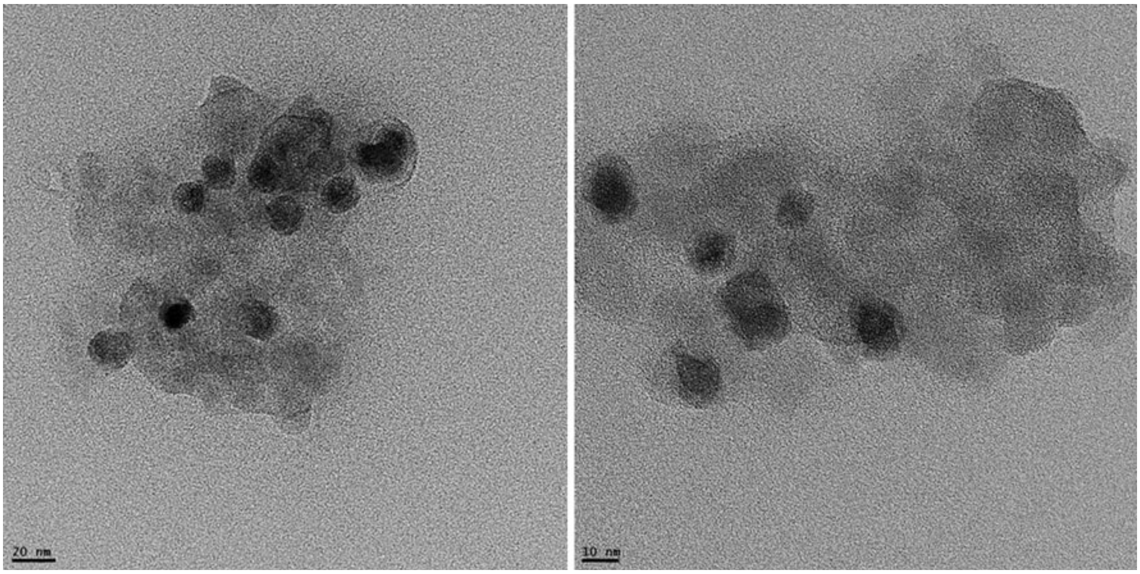

Fig. 1 TEM of the 3.57 wt% Fe/SiO$_2$ sample

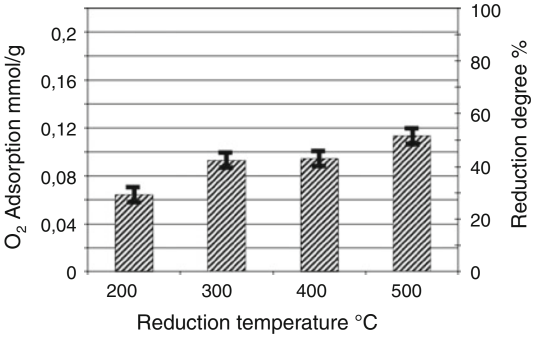

Fig. 2 Oxygen amounts adsorbed per gram of sample at 400 °C by the 1.62 wt% Fe/SiO_2 solid and the corresponding Fe reduction degree (%) as a function of the reduction temperature

reduction temperature with the total theoretical amount of oxygen it could consume (total conversion of Fe^0 to ferric oxide). It appears that the reduction degree of iron increased slightly with the reduction temperature in a range between 30 and 50 % confirming that pure iron is difficult to reduce (Fig. 2). These results are consistent with some reported in the literature; for instance Niemantsverdriet observed during TPR up to 500 °C that Fe was not reduced more than 30–40 % [12].

3.2 Rh–Fe/SiO_2 and Rh–^{57}Fe/SiO_2 Bimetallic Catalysts

The following catalyst preparations were obtained: 3.57 wt% Fe, 0.25 wt% Rh; (Fe/Rh = 26); 5.44 wt% ^{57}Fe, 0.16 wt% Rh; (^{57}Fe/Rh = 63) (see "Experimental" section) and characterized.

3.2.1 Electron Microscopy

TEM of Rh–Fe/SiO_2 sample (Fe/Rh = 26) revealed a heterogeneous size distribution ranging from 20 to 50 nm (Fig. 3).

3.2.2 X-Ray Diffraction

The XRD pattern of the previous Rh–Fe/SiO_2 sample (Fe/Rh = 26) after reduction under hydrogen at 450 °C is shown in Fig. 4. It shows the presence of iron (88 %), Rh (5 %) and Fe_9Rh_1 alloy (7 %). However, from these values, an average Fe/Rh molar ratio of 12 could be calculated, instead of 26 given by elemental analysis. This indicates that some Fe particles could not be detected by this method and were amorphous or well-dispersed in very small clusters not detectable by XRD; indeed, this method requires a minimum particle size to proceed.

3.2.3 Oxygen Uptake

In order to check a possible effect of rhodium on the reducibility of iron, the oxygen uptake on the Rh–Fe/SiO_2 (Fe/Rh = 26) catalyst treated under flowing hydrogen at various temperatures was measured, according to the procedure described in experimental section. Fig. 5 shows the amount of oxygen consumed by the Rh–Fe/SiO_2 (Fe/Rh = 26) solid and thus the total reduction degree for increasing reduction temperatures from 200 to 500 °C. The extent of reduction increased with the reduction temperature to reach about 90 % at 500 °C. Therefore, it appeared clearly that iron

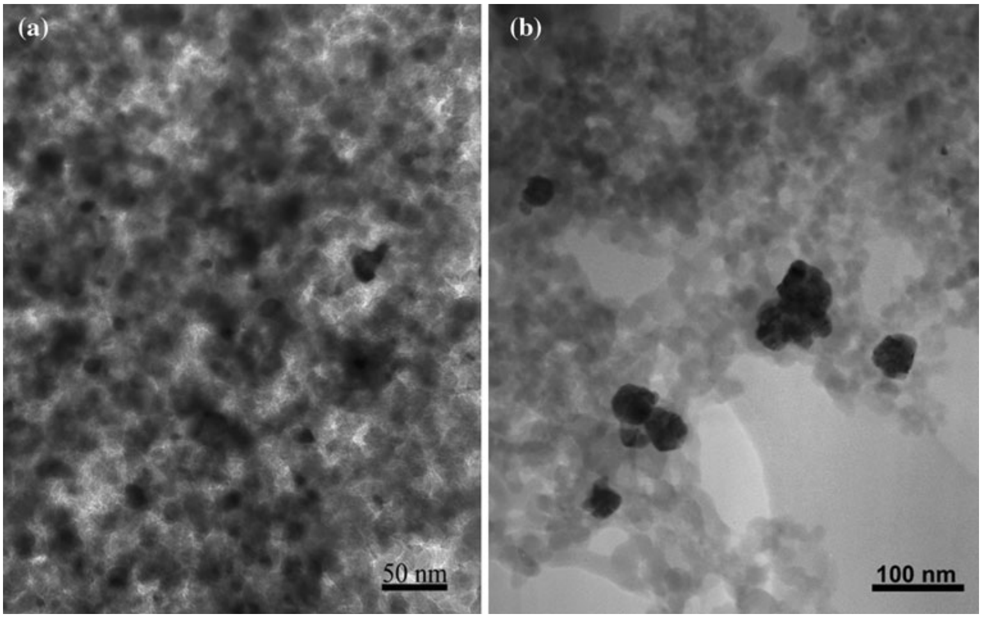

Fig. 3 TEM of the Fe–Rh/SiO_2 (Fe/Rh = 26) sample

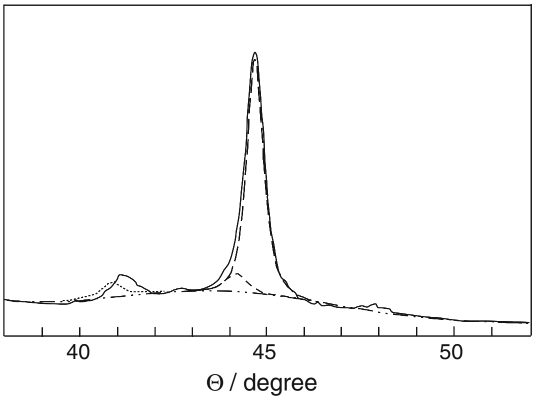

Fig. 4 X-ray diffraction of the Fe–Rh/SiO$_2$ sample (Fe/Rh = 26) at 25 °C under H$_2$ after reduction at 450 °C and its deconvolution ((*line*) diffractogramm; (*large dashed line*) Fe; (*small dashed line*) Fe$_9$Rh$_1$; (*dotted line*) Rh)

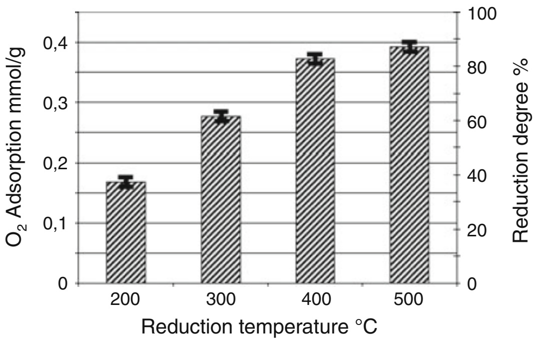

Fig. 5 Quantity of oxygen adsorbed per gram of sample at 400 °C by the Fe–Rh/SiO$_2$ solid (Fe/Rh = 26) and the corresponding total reduction degree (%) as a function of the reduction temperature

was more deeply reduced in the presence of even a small amount of rhodium. Such phenomenon has already been reported in the literature for comparable amounts of Fe and Rh [12] and also with other couples involving a noble metal: Fe–Ru [18], Fe–Pt [20] or Fe–Pd [21].

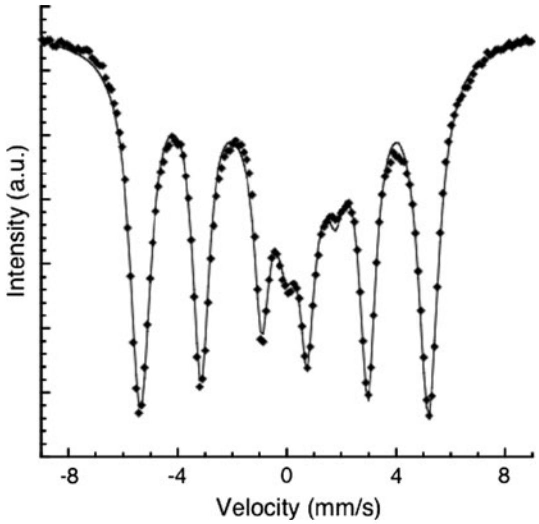

Fig. 6 Mössbauer spectrum of the ^{57}Fe–Rh/SiO$_2$ sample, recorded at 25 °C after a second reduction at 500 °C; the solid line is derived from least-square fit

3.2.4 Mössbauer Spectroscopy

In order to better investigate the evolution of iron oxidation states during the thermal treatments under hydrogen, at different temperatures, Mössbauer spectroscopy was used with a 98 % ^{57}Fe-enriched Rh–^{57}Fe/SiO$_2$ catalyst (Fe/Rh = 63) (Table 1). At the difference of X-ray diffraction, Mössbauer spectroscopy enabled to detect all the iron species present on the support. To illustrate the results, the spectrum of the sample after a second reduction at 500 °C which was the most reduced sample obtained, is presented in Fig. 6. All spectra of the reduced catalysts consist of a doublet and a sextet that can be attributed respectively to Fe^{2+} and Fe^0 species (Table 1). The hyperfine parameters of the sextet are those of pure α-iron although the internal magnetic field appeared slightly lower (32.7 instead of 33.3 T).

Table 1 ^{57}Fe absorption Mössbauer hyperfine parameters calculated from the fitting of the spectra recorded at 25 °C

Successive conditionings	δ (mm/s)	Δ (mm/s)	H (T)	Relative intensity (%)	Attribution	Total reduction degree (%)[a]
H$_2$/400 °C	−0.01	0.00	327	64	Fe^0	77
	1.01	1.83	–	36	Fe^{2+}	
H$_2$/500 °C	0.00	0.00	326	90	Fe^0	93
	0.99	1.83	–	10	Fe^{2+}	
O$_2$/400 °C	0.32	1.28	–	100	Fe^{3+}	
H$_2$/300 °C	0.00	0.00	328	77	Fe^0	85
	0.98	1.90		14	Fe^{2+}	
	0.88	1.10		8	Fe^{2+}	
H$_2$/500 °C	0.00	0.00	327	93	Fe^0	95
	0.98	1.80		7	Fe^{2+}	

[a] The total reduction degree is the ratio of the measured oxygen uptake to the maximum theoretical amount the catalyst can consume

δ isomer shift (referred to α-Fe), Δ quadrupolar splitting, *H* internal magnetic field

The average Mössbauer parameters of the doublet indicate that the coordination of the Fe^{2+} ions was tetrahedral or octahedral with a strong distortion. The reduction extent which could be deduced from the concentration of these species fitted roughly with the values obtained from oxygen adsorption, i.e. around 90–95 % after treatment at 500 °C. All iron species were re-oxidized to Fe^{3+} by a subsequent treatment under O_2 at 400 °C. The hyperfine parameters of the detected doublet were typical of those measured when ferric oxide was distributed at the surface of silica [30]. Upon re-reduction, the same Fe^{2+} and Fe^0 species were observed. As already described in literature [31], a second reduction treatment at this stage produced a deeper reduction of iron at similar temperature; for instance, Fe was reduced up to 85 % at 300 °C while oxygen adsorption gave a 61.5 % value for the same temperature in the first reduction run.

3.2.5 *Effect of the Fe/Rh Ratio on the Reducibility of Iron*

In order to test the extent of the promoting effect of Rh on the reducibility of Fe, a series of catalysts with increasing Fe/Rh ratio up to the value 2,000 were prepared, starting from the 3.57 wt% Fe/SiO_2 solid. All these catalysts were reduced at 500 °C under hydrogen flow and the reduction degree determined with the subsequent oxygen uptake. It turned out that even with the higher Fe/Rh ratio, the reduction extent of Fe remained in the same range of values around 80–95 % as observed at lower ratio (Fig. 7). These results thus indicate that a very small amount of rhodium proves sufficient to promote the almost complete reduction of iron. Again, it turned out that a second reduction leads to an increased reduction degree of iron (Fig. 7: see lozenges and discs). Note that for a 30 nm diameter particle, the number of Fe atoms is about 1.000.000. Even for the ratio Fe/Rh = 2,000, a 30 nm iron particle may contain approximately 500 Rh atoms. Since most of the iron particles are around 30 nm, the probability to have some Rh atoms in each one is rather high. However, if we consider the hypothesis that some iron particles may not be in contact with rhodium atoms then the promoting effect should involve an indirect way and possibly use the transfer of activated hydrogen through the usually called hydrogen spillover effect [32]. This phenomenon is common in heterogeneous catalysis and has been observed on various supported rhodium catalysts such as Rh/SiO_2, Rh/Al_2O_3, Rh/TiO_2, Rh/CeO_2 [33–36]. To check the possibility of a spillover effect, a physical mixture of Fe/SiO_2 and 0.4 wt% Rh/SiO_2 (Fe/Rh = 2,000) was also prepared by mixing the two powders; recall that before mixing Rh/SiO_2 was reduced at 500 °C under hydrogen which would prevent Rh migration; since the Fe/Rh ratio is very high, most of Fe could not be in contact with Rh particles. In this case again, the reduction degree of Fe proved high (Fig. 7, open square symbol), supporting the occurrence of a hydrogen spillover through the solid.

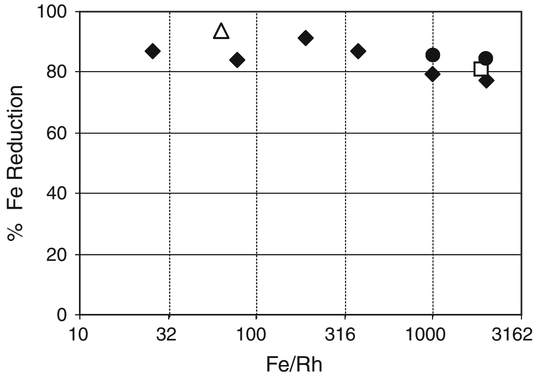

Fig. 7 Evolution of the iron reduction degree under H_2 at 500 °C as a function of the Fe/Rh ratio in $Fe–Rh/SiO_2$ catalysts (in logarithmic scale); *filled diamond* first reduction run; *filled circle* second reduction run; *open triangle* $^{57}Fe–Rh/SiO_2$ sample; *open square* $Fe/SiO_2 + Rh/SiO_2$ physical mixture

4 Conclusion

The reducibility by hydrogen of Fe/SiO_2 and $Rh–Fe/SiO_2$ with only a very low Rh content has been studied by oxygen adsorption and Mössbauer spectroscopy. Whereas Fe/SiO_2 cannot be reduced to more than 50 % within the temperature range between 200 and 500 °C, the presence of even a small amount of Rh (Fe/Rh $\leq$ 2,000) promotes the reduction of iron at 500 °C, up to 85–95 %. The promoting effect also takes place with a $Fe/SiO_2 + Rh/SiO_2$ physical mixture (Fe/Rh $\leq$2,000) which suggests the occurrence of a hydrogen spillover process. Such effect may also take place in the other bimetallic Fe–Rh catalysts.

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