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Morphological and structural changes in reducing and steam atmospheres of SiO_2-supported Rh catalysts

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Reduced centres are formed at the silica surface during the pretreatment of Rh/SiO_2 catalysts at high temperatures (500–900°C). These centres can be titrated with steam according to the reaction: reduced centre + $H_2O \rightarrow$ oxidized centre + H_2. The selective formation of H_2 when catalysts pretreated in D_2 are reacted with H_2O confirms that steam is decomposed during the titration reaction. XRD, TEM and EDX were used to investigate the morphological and structural changes in the catalysts. Owing to the formation of Rh_2Si alloy, the number of reduced centres formed on SiO_2 is much greater than the number found with Rh/Al_2O_3 reduced under similar conditions.

Keywords: metal support interactions, support reduction, Rh/SiO_2 catalysts

1. Introduction

High-temperature reduction of supported metal catalysts can cause profound changes in the metal surface areas, in the surface composition and in the particle morphology. High-temperature treatments can also create structural and chemical modifications of the support, particularly in the vicinity of metal particles. Supports inducing strong metal–support interactions (SMSI) can be reduced or oxidized under mild conditions, particularly in the presence of metals [1]. Duprez et al. [2] proposed a technique for measuring the number of reduced centres of TiO_2 in Rh, Pt and Ni/TiO_2 catalysts. This technique is based on the measurement of the amount of H_2 produced by oxidation with H_2O pulses in accordance with the following equation:

$$V_{O^{2-}} + H_2O + 2e^- \rightarrow O^{2-} + H_2 \qquad (1)$$

where $V_{O^{2-}}$ is an anion vacancy and $2e^-$ represents electrons delocalized in the conduction band of TiO_2 (reduced state). The use of steam, instead of O_2, for the oxidation of these reduced centres presents two main advantages:

(a) the reaction is selective: only the reduced centres of the support are oxidized, while the metals remain essentially in their reduced state;

(b) hydrogen can be detected with a very high sensitivity.

This technique was applied successfully to Rh and Pt/Al_2O_3 catalysts [3]. We showed that defect centres, rather than reduced centres, were formed on alumina, in the close proximity of the metal particles. We report here the results of an investigation carried out on silica-supported rhodium catalysts.

2. Experimental

2.1. Catalyst preparation

Rhône-Poulenc DBM200 silica (250 $m^2\ g^{-1}$) was used as a carrier. The catalysts were prepared by wet impregnation of the support with aqueous solutions of $RhCl_3{\cdot}3H_2O$. After impregnation the catalysts were dried overnight at 120°C and then calcined in air at 450°C for 4 h. The samples were characterized by H_2 chemisorption (H_C), oxygen titration (O_T) and hydrogen titration (H_T) carried out in a chromatographic reactor described previously [4].

2.2. H_2 reduction and H_2O titration

The sample (0.2 g) was heated at 10°C min^{-1} under a flow of ultrapure H_2 (20 $cm^3\ min^{-1}$; less than 1 ppm of impurities) up to the reduction temperature T_R. It was maintained at this temperature for 1 h and then purged under a flow of ultrapure Ar (20 $cm^3\ min^{-1}$; < 1 ppm impurities) for 30 min and cooled down to the temperature of oxidation by steam T_{ox}. Pulses of steam (56 μmol H_2O) were then injected on the catalyst sample every ten

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minutes. H_2 was analyzed by gas chromatography on a 5A molecular sieve column coupled with a thermal conductivity detector. We observed that the amount of H_2 decreased rapidly as a function of the number of pulse and then stabilized at a very low value after the fourth pulse of water. The same procedure was used for the experiments in which both the temperature of reaction with steam was varied and the temperature of reduction was fixed.

2.3. H/D isotopic labelling

H_2 formation upon H_2O injection could result from some hydrogen stored in the catalyst during its reduction. To check this, a H/D isotopic labelling study was carried out. The sample was reduced in D_2 for 30 min and purged in Ar for 30 min. Pulses of water (H_2O) were then injected. The effluents were analyzed by mass spectrometry (Balzers QMG 420) coupled with the gas chomatographic apparatus via a capillary connection system. The mass spectrometer response was corrected from the differences in the ionization probability and in the capillary diffusivity of H_2, HD and D_2.

2.4. X-ray diffraction

XRD analyses were carried out in a Siemens D500 powder diffractometer using Cu $K\alpha_1$ radiation (0.15406 nm). About 50 mg of catalyst were pressed in the sample holder. The crystalline phases were identified by comparison with JCPDS files: Rh metal (05-685), SiO_2 cristobalite (39-1425) and Rh_2Si alloy (37-1416).

2.5. Transmission electron microscopy and energy-dispersive X-ray analysis

TEM was performed in a Philips CM120 microscope with a resolution of 0.35 nm. The sample was crushed, ultrasonically suspended in ethanol, deposited on a Cu grid previously covered with a thin layer of carbon. EDX element analyses were carried out in the STEM mode of the microscope using a Si(Li) Super UTW detector with a resolution of 148.5 eV. In order to minimize the contribution of the support, only the particles located on the edges of the silica patches were analysed by EDX.

3. Results

3.1. Characterization of the fresh catalysts

The results of the chemisorptions (H_C) and of the titrations (O_T, H_T) carried out on the fresh catalysts reduced at 400°C are reported in table 1. This table also gives the values of the metal dispersions calculated by $\%D = 100\ Hc/M_t$, where Hc is the number of chemisorbed hydrogen atoms and M_t the number of metal atoms in the sample.

Table 1
Dispersion measurements of the fresh catalysts reduced at 400°C for 16 h. Hydrogen and oxygen uptakes are given in μmol at. g^{-1}

Catalyst	wt% metal	μmol Rh g^{-1}	H_C	O_T	H_T	%D
$4Rh/SiO_2$	4.12	400.3	51	86	177	13
$0.4Rh/SiO_2$	0.38	36.9	4.6	6.6	19.0	12

3.2. H_2O titration: effect of T_R on H_2 production ($T_{ox} = 500°C$)

The effect of the reduction temperature T_R on the number of reduced centres, as determined by the H_2O titration technique, was investigated. Figure 1 shows the cumulative amounts Q_H of H_2 produced during the titration at $T_{ox} = 500°C$ (five pulses of H_2O). Q_H, very low on the samples reduced at 500°C, increases rapidly with T_R. Figure 1 also shows that Q_H depends strongly on the metal loading. In separate experiments, it was proved that the bare support treated in H_2 at high temperature (800–900°C) could not decompose the water molecule. This shows that the metal-free silica surface is little or not upset under these conditions.

The $4Rh/SiO_2$ catalyst sample has been characterized by H_2 chemisorption before (just reduced at T_R for 1 h) and after H_2O titration. The results (table 2) clearly indicate that the high-temperature (HT) reduction suppresses the ability of the catalyst to chemisorb hydrogen while H_2O titration restores the initial properties of the catalyst, either totally ($T_R < 800°C$) or partially ($T_R > 800°C$). This is indicative of a strong metal–support interaction (SMSI) effect as reported earlier by Tauster et al. in the case of TiO_2-supported catalysts [1]. This annihilation by H_2O of the SMSI effect is comparable to what was observed with oxygen [5–7].

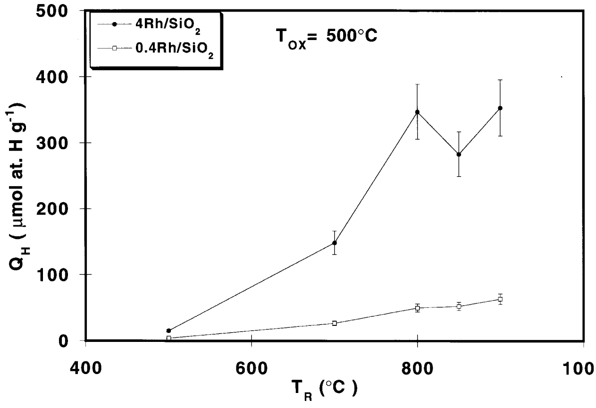

Figure 1. Overall amount of H_2 formed in H_2O titration (five pulses) over Rh/SiO_2 as a function of the reduction temperature T_R.

Table 2
H_2 chemisorption on the $4Rh/SiO_2$ catalyst (a) before H_2O titration (1 h at T_R), (b) after H_2O titration at 500°C (without any further reduction)

T_R (°C)	T_{ox} (°C)	H_C (a) (μmol at. g^{-1})	H_C (b) (μmol at. g^{-1})
700	500	9.2	51.3
800	500	0	47.5
850	500	0	24.0
900	500	0	5.1

High-temperature reduction (1 h in H_2) induces a significant sintering of the metal particles above 800°C (table 2), which can explain the minimum of Q_H observed at 850°C (figure 1). The amount of reduced sites created on the support depends both on the rate of hydrogen flux F_H across the metal/support interface and on the intrinsic rate R_{red} of formation of these reduced sites. Only F_H (proportional to the specific perimeter of the metal particles) depends on the metal sintering. When T_R is increased, F_H decreases significantly above 800°C while R_{red} increases continuously, depending only on the activation energy of the surface reduction reaction. Owing to the balance between these two processes, Q_H first decreases between 800 and 850°C (determining effect of F_H) before increasing again above 850°C (determining effect of R_{red}).

3.3. H_2O titration: effect of T_{ox} on H_2 production ($T_R = 850°C$)

The variations of Q_H with the temperature of H_2O titration are shown in figure 2. For a given catalyst and for the same temperature of reduction (850°C), the amount of hydrogen produced in titration slightly increases with T_{ox}. Apparently, part of the sites created by reduction at 850°C are not easily titrated by H_2O. The $Q_H(500)/Q_H(900)$ ratio amounts to 65% for $0.4Rh/SiO_2$ and 75% for $4Rh/SiO_2$. Moreover, it seems that not all the reduced sites can be titrated at 900°C, which proves that certain sites are deeply embedded in the silica matrix.

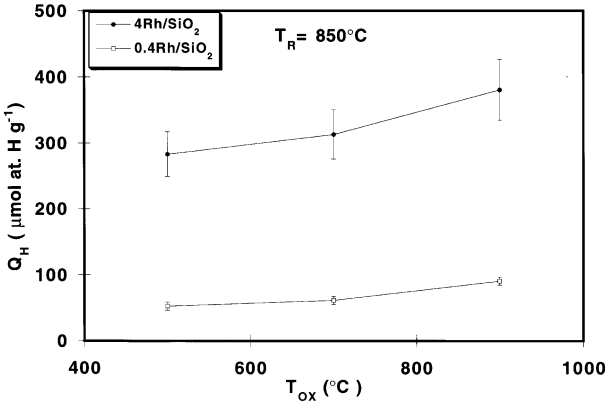

Figure 2. Overall amount of H_2 formed in H_2O titration (five pulses) over Rh/SiO_2 as a function of the titration temperature T_{ox}.

Hydrogen chemisorptions were carried out after titration (table 3). Keeping in mind that there was no hydrogen uptake on the catalyst merely reduced at 850°C (not yet titrated), the data of table 3 confirm that H_2O titration allows the catalyst to recover a significant part of its chemisorption properties. However, titration above 700°C is accompanied with a definite sintering of the catalyst which adds to the sintering due to the high-temperature reduction.

3.4. H/D isotopic labelling

H_2O decomposition on reduced silica centres is the most likely hypothesis for explaining the H_2 formation in H_2O titration. Another plausible hypothesis is the desorption, by water, of the hydrogen which could have been stored in the catalyst during HT reduction. Figure 3 shows the isotopic analysis of the hydrogen produced by reaction of H_2O on a catalyst sample reduced in D_2. The production of H_2 is definitely greater than that of HD of D_2, which confirms the first hypothesis (H_2O decomposition). Moreover, HD and D_2 can be formed possibly via a secondary reaction of exchange between H_2 and the OD groups of silica. Nevertheless, the fact that D_2 is the first isotopomer to be formed in the reaction (see the first pulse in figure 3) implies that the second hypothesis (D_2 desorption) cannot be definitely discarded.

3.5. X-ray diffraction

The 4% Rh/SiO_2 catalyst was examined by XRD after different treatments: reduction at 500°C ($4Rh/SiO_2R500$), reduction at 980°C ($4Rh/SiO_2R980$) and steam-treatment at 980°C after reduction at that temperature ($4Rh/SiO_2R980H_2O980$). Rh metal is the only rhodium species detected in the sample reduced at 500°C (figure 4a). In $4Rh/SiO_2R980$, the peaks corresponding to the cfc structure of Rh disappear while a new phase identified as Rh_2Si can be observed (figure 4b). This rhodium silicide has an orthorhombic structure ($a = 0.5410$ nm; $b = 0.3928$ nm and $c = 0.7388$ nm). It reacts with steam at 980°C and reforms metallic rhodium and a well-crystallized SiO_2 having the cristobalite

Table 3
H_2 chemisorption on the $4Rh/SiO_2$ catalyst after H_2O titration at different temperatures. There is no hydrogen uptake on the catalyst reduced at 850°C before H_2O injection

T_R (°C)	T_{ox} (°C)	H_C (μmol at. g^{-1})
850	700	24.0
850	800	23.1
850	900	12.2

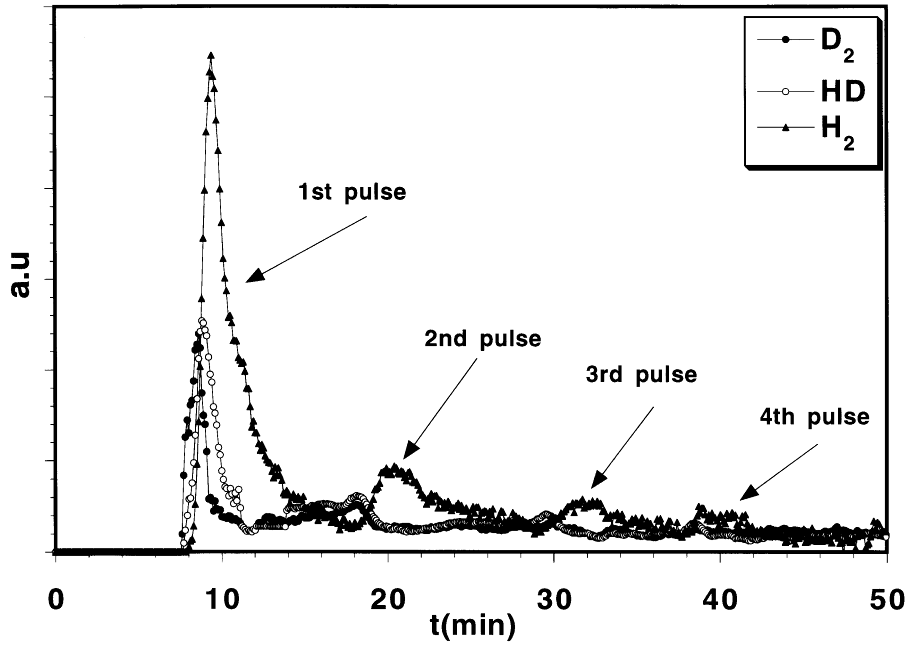

Figure 3. H_2, HD and D_2 formation upon H_2O pulses over 4Rh/SiO_2 reduced in D_2.

structure (figure 4c). It is worth noting that the steam treatment at 980°C has not entirely destroyed the rhodium silicide. The mean particle size of rhodium in 4Rh/SiO_2R500 is 6.7 nm, which corresponds to a 14% dispersion, a value very close to that found by H_2 chemisorption for the fresh catalyst (table 1). XRD also shows that HT treatments lead to a sintering of rhodium: the mean size of Rh_2Si particles is 11.5 nm in 4Rh/SiO_2R980 while that of Rh in 4Rh/SiO_2R980H_2O980 would be 17.2 nm. Similar diffractograms were obtained with the catalyst reduced or oxidized at a lower temperature. However, owing to a smaller particle size in these samples, the different XRD peaks were not so well-resolved as in the diffractograms of figure 4.

3.6. *Electron microscopy and energy-dispersive element analysis*

Figure 5 shows representative micrographs of the 4Rh/SiO_2 catalyst after different treatments. In 4Rh/SiO_2R500 (figure 5a), most Rh particles have a three-dimensional, spherical shape, in agreement with pre-

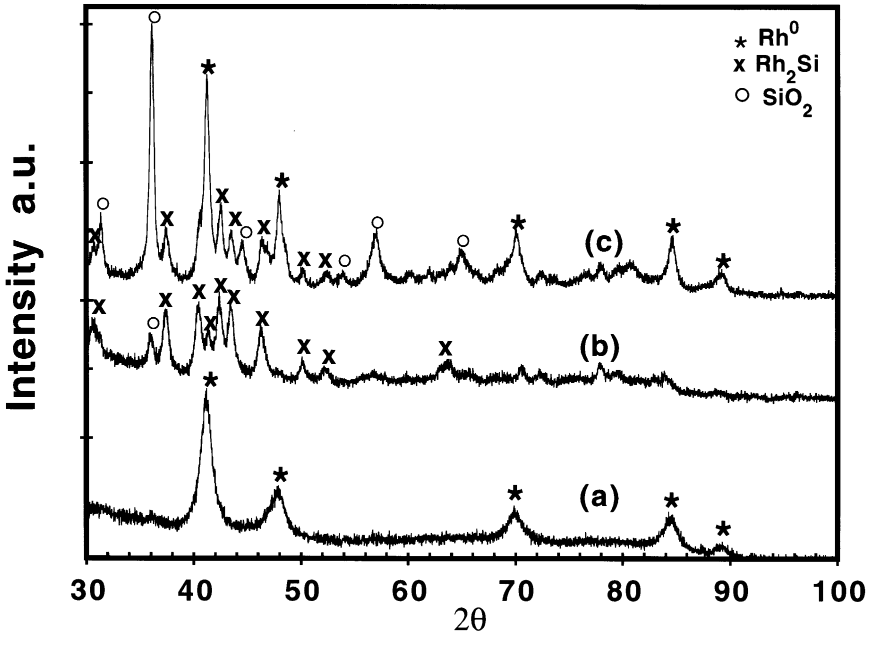

Figure 4. X-ray diffractograms of 4Rh/SiO_2 catalyst: (a) 4Rh/SiO_2R500, (b) 4Rh/SiO_2R980, (c) 4Rh/SiO_2R980H_2O980.

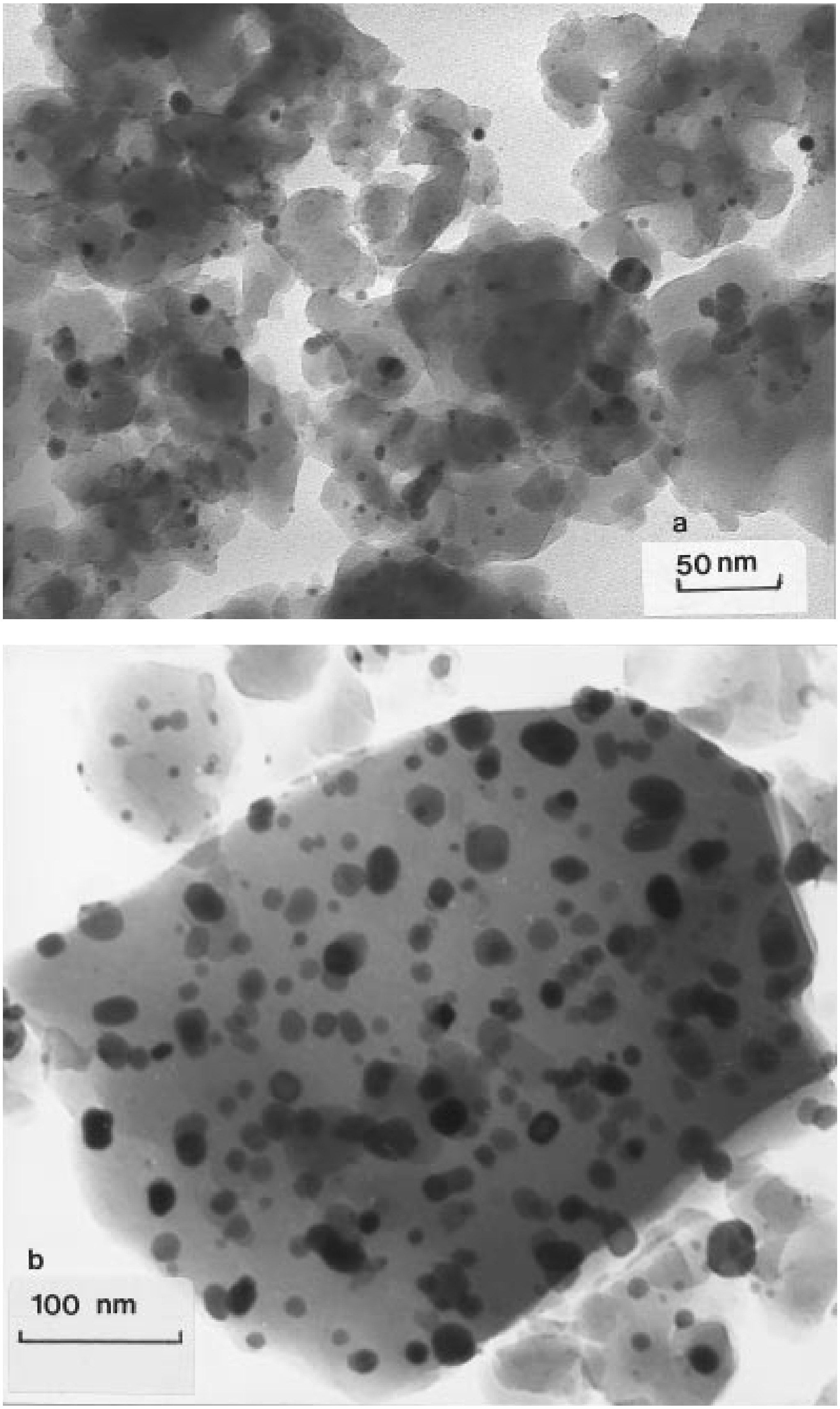

Figure 5. TEM micrographs of $4Rh/SiO_2$ catalyst: (a) $4Rh/SiO_2R500$, (b) $4Rh/SiO_2R980$, (c) $4Rh/SiO_2R980H_2O980$. (Continued on next page.)

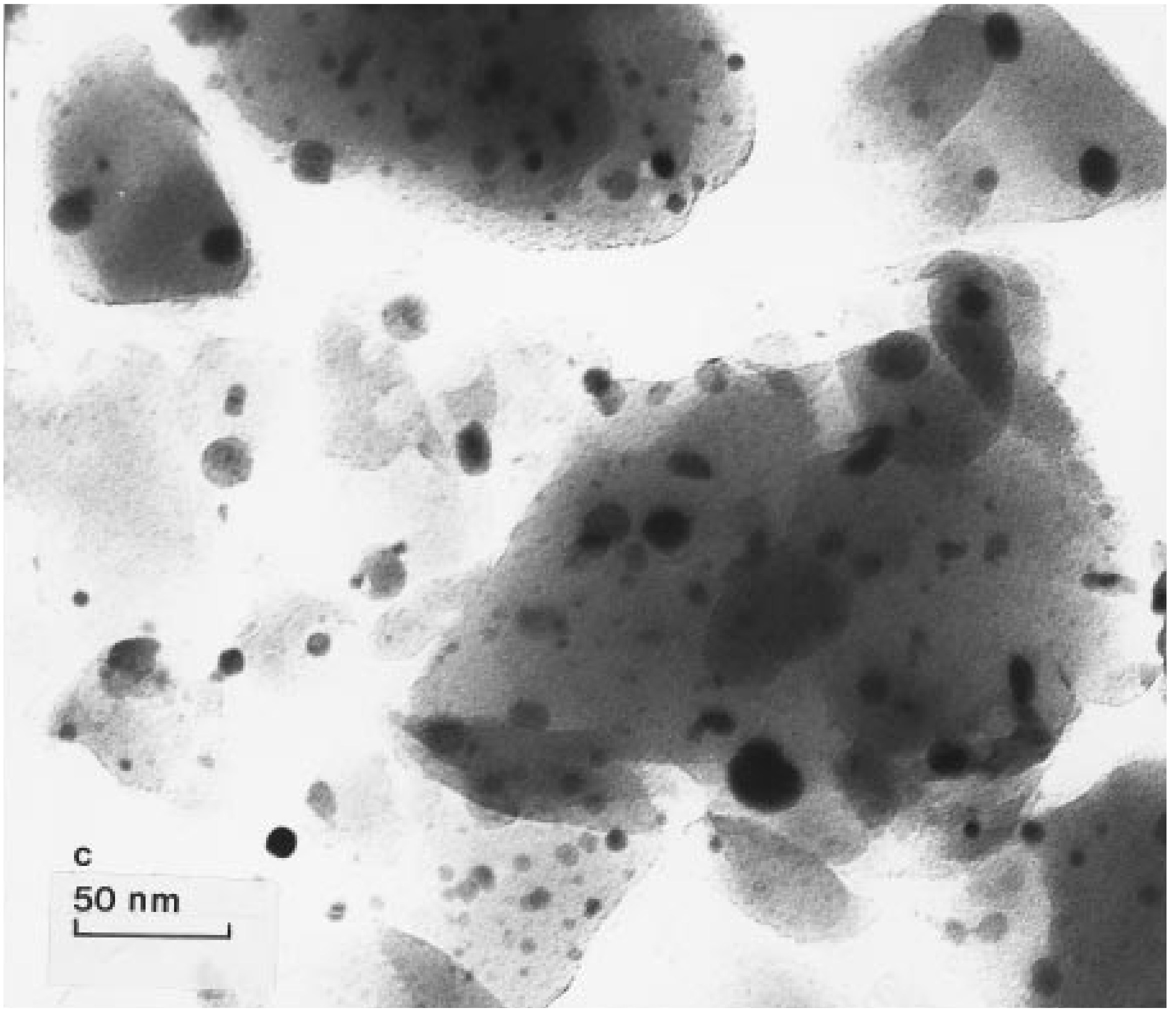

Figure 5. (Continued.)

vious observations of Chakraborti et al. [8]. In 4Rh/SiO_2R980 (figure 5b), a definite morphological change can be observed: numerous particles have a hexagonal shape, which can be related to the structural change ($Rh^0 \rightarrow Rh_2Si$) induced by the high-temperature reduction. Moreover, an apparent spreading of the silicide particles on the support leads to low-contrast bidimensional crystallites. After the steam treatment at 980°C, most particles recover their initial spherical shape (figure 5c). However, certain particles seem to retain a hexagonal shape. This can be attributed to the presence of residual Rh_2Si particles or to a preferential (111) orientation of the rhodium particles [9].

Table 4
Normalized EDX atomic percentages of Rh and Si in the particles of 4Rh/SiO_2 after different treatments

Catalyst	%Rh (K_α)	%Si (K_α)	Rh/Si ratio
4Rh/SiO_2R500	47	53	0.886
4Rh/SiO_2R980	19.5	80.5	0.242
4Rh/SiO_2R980H_2O980	44.6	55.4	0.805

EDX analysis was carried out to obtain information on the composition of the particles after the different treatments. In each case, ten particles were analysed, the mean composition being given in table 4. It has not been possible to eliminate the contribution of the support in the X-rays emitted from the selected area. However, the particles formed after high-temperature reduction have a high silicon content, which shows the formation of a new compound between rhodium and silicon. The EDX analysis confirms that this compound is destroyed by steam at 980°C and that the initial composition is restored.

4. Discussion

This study has shown that a reduction of Rh/SiO_2 catalysts in H_2 above 500°C led to the appareance of reduced centres on the silica support. These reduced centres were analyzed by H_2O titration according to the reaction:

$$\text{reduced centre} + H_2O \rightleftharpoons \text{oxidized centre} + H_2 \qquad (2)$$

The experiments performed with the catalyst reduced in a flow of D_2 showed that the formation of H_2 was essentially due to the decomposition of water. A significant production of H_2 was observed with the Rh/silica catalysts and it was shown that Q_H increased significantly with the temperature of reduction T_R and slightly with the temperature of titration T_{ox}.

These results contrast with those obtained with Al_2O_3-supported catalysts [3], for which the amounts of H_2 produced in H_2O titrations depended little on T_R and T_{ox} (figure 4). This was attributed to a limited number of reducible centres of Al_2O_3, exclusively located at the periphery of the metal particles. We showed that the number of Al ions in contact with the metal particles was approximately the third of the amount of H atoms produced in H_2O titration.

The significant increase of Q_H with T_R shows that the reduction of silica is not limited to the silicon ions in close contact with the rhodium particles. As the presence of the metal is required for reducing the support, it can be concluded that a relatively large area of silica surrounding the rhodium particles is reduced after the HT treatment in H_2. The silicon thus formed can react with the rhodium to form intermetallic compounds. The presence of an Rh_2Si alloy in the $4Rh/SiO_2$ catalyst reduced at high temperature was proved by XRD while TEM showed relatively flat alloy particles spread on the support. The formation of this rhodium silicide compound implies the reduction of SiO_2 in the presence of Rh and H_2:

$$2Rh + SiO_2 + 2H_2 \rightleftharpoons Rh_2Si + 2H_2O \tag{3}$$

The formation of metal silicide compounds has been observed by different authors. Praliaud and Martin [10] reported that the activity of Ni/SiO_2 in benzene hydrogenation dramatically decreased after reduction of the catalyst sample at 850–900°C. Magnetic measurements revealed that the sample reduced at high temperature behaved as a Ni–Si alloy with a 11.5 at% Si composition. Juszczyk and Karpinski [11,12] detected, by XRD, the formation of palladium silicides (Pd_3Si and possibly Pd_5Si) in Pd powder mixed with silica after high-temperature reduction at 600°C. However, similar experiments carried out with Pd/SiO_2 catalysts suggested the presence of Pd_2Si after HT reduction [11]. Romanovsky and Lamber [13,14] used electron diffraction to show that Pt–Si alloys (mainly Pt_2Si) were formed when thin films of Pt deposited on quartz glass substrates were reduced at temperatures as low as 550°C. During the formation of these Pt–Si alloys, Romanovsky and Lamber noticed a "wetting" of the quartz surface by platinum, a phenomenon similar to what we observed with the $4Rh/SiO_2R980$ catalyst. Microdiffraction analysis also showed the formation of palladium silicide (Pd_2Si) on Pd/SiO_2 films treated in H_2 (10^{-2} Pa) at 572°C [15]. These authors noticed that alloy formation was enhanced on hydroxylated silica surface, the reduction of silanol groups (eq. (4)) being less demanding energetically than the reduction of silica (eq. (5)):

$$2Pd + SiOH + \tfrac{1}{2}H_2 \rightleftharpoons Pd_2Si + H_2O \tag{4}$$

$$2Pd + SiO_2 + 2H_2 \rightleftharpoons Pd_2Si + 2H_2O \tag{5}$$

Wong and Mc Cabe [16] did not observe any formation of new Rh–Si compounds after the reduction of their 1% Rh/SiO_2 catalyst in a flow of H_2 at 800°C. This is probably due to the oxidative post-treatment at 450°C applied to the catalyst before characterization. H_2O titration leads partly to the re-oxidation of reduced silica and to the reformation of rhodium particles. XRD, TEM and EDX showed that the Rh_2Si alloy crystallites were destroyed. Moreover, the chemisorptive properties of the metal were restored and no peak of Rh_2O_3 was observed in the XRD spectra of the water-treated catalysts. This confirms that the noble metal is not oxidized by H_2O during the titration reaction. The effect of water on catalysts exhibiting SMSI phenomena was investigated by Baker et al. in the case of Pt/TiO_2 specimens (films and powder) [7,17]. Water at 250°C annihilates SMSI effects and partly restores H_2 and CO chemisorption. Titania-supported catalysts have been the subject of in-depth studies, as a model of solids giving rise to SMSI effects. These effects are evident in catalysts reduced at relatively moderate temperatures (400–500°C). Titanium suboxides, such as Ti_4O_7, are then formed [17,18] and the noble metal can be deeply embedded in the reduced titania matrix [19–22]. However, an electron transfer from the titania suboxide to the noble metal accompanies the HT reduction [21,23] and, under certain conditions, direct Rh–Ti bonding was shown by XANES in Rh/TiO_2 catalysts reduced at 500°C, which suggested the formation of new structures resembling RhTi or Rh_3Ti [24]. In the case of silica-supported catalysts, the formation of silica suboxides seems very unlikely and H_2 reduction leads to intermetallic compounds above 500°C. Once formed, the rhodium silicide appears to be relatively stable: H_2O titration has

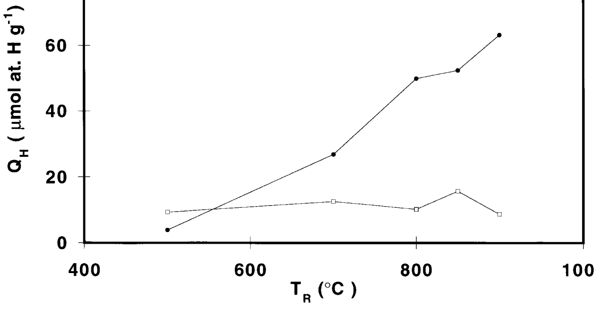

Figure 6. Amount of H_2 formed in H_2O titration at 500°C. Comparison between Al_2O_3- and SiO_2-supported Rh catalysts.

to be carried out at high temperatures to obtain a significant re-oxidation of the silicon in these rhodium silicides. Other studies are in progress to examine the effects of HT reduction and of H_2O titration on the catalytic activity of these Rh/SiO_2 catalysts.

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