Chloride-induced migration of supported platinum and palladium across phase boundaries

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Previous work showed that calcination in O_2 of physical mixtures of Fe_2O_3 and supported Pt leads to a strong reduction enhancement of the Fe_2O_3, but that a much smaller effect was observed with supported Pd. The present results show that a strong reduction enhancement could be achieved by pretreating Pt/Al_2O_3 or Pd/Al_2O_3 with NH_4Cl and then decomposing NH_4Cl, before mixing the solid with Fe_2O_3. Such pretreatment with NH_4Cl has no effect on SiO_2 or zeolite-supported metals, because only Al_2O_3 retains chloride ions at its surface. In the physical mixtures, chlorides migrate from Al_2O_3 to Fe_2O_3 at elevated temperature and form a volatile compound, presumably $FeCl_3$. Layered-bed experiments show that this $FeCl_3$ sublimes, and that its chemical interaction with Pt or Pd on any support results in the formation of mobile Pt– or Pd–chloro complexes that reach Fe_2O_3 particles by surface migration. After exposure to an H_2 flow, the complexes are reduced, and Pt or Pd particles are formed on the Fe_2O_3, enhancing its reduction by H spillover. These metal particles on the Fe_2O_3 have been identified by TEM and X-ray energy dispersive spectroscopy (EDS). Abundant formation of PdFe alloys upon reduction is verified by TPR/TPD, indicating that almost all Pd has interacted with the volatile Fe chloride. In the absence of a transition metal, chloride ions retard the reduction of Fe_2O_3.

Keywords: surface migration, catalyst regeneration, platforming catalysts, metal redistribution, reduction enhancement, hydrogen spillover, PdFe alloy formation

1. Introduction

Various authors have investigated the mechanism of platinum redispersion and agglomeration on the surface of oxide supports (see [1–3]). Under oxidizing conditions chlorides are known to facilitate platinum redispersion [4,5], which is attributed to the formation of chlorinated platinum compounds; yet no participation of a chlorinated support has been considered. Recently, Zhang and Beard reported that, under reducing conditions, agglomeration of platinum in Pt/Al_2O_3 is enhanced if the catalyst is pretreated with NH_4Cl [6,7]. The authors assume that some chlorination of the support occurs in this process, yet no data seem to exist in the open literature on the effect of chlorides on the migration of Pt or other transition metals across the phase boundary between their support and a different oxide. The objective of this present work is to clarify this process.

In our previous work [8,9], temperature-programmed reduction (TPR) of Fe_2O_3 in mixtures with metal-containing zeolites and EDS were used to detect and study the migration of transition metals and their oxides or ions out of zeolites onto the iron oxide. It was found, for instance, that platinum oxide is much more mobile than reduced metal particles, and that "hydrogen spillover" along the walls of the zeolite channels was negligible. In the present work the same technique will be used to study the effect of a treatment with NH_4Cl on the mobility of Pt and Pd across the boundary between alumina or silica and iron oxide.

2. Experimental

Silica gel from Aldrich, γ-alumina from BDH Chemicals Ltd. and zeolite NaMFI with $\mathrm{Si:Al} = 13.5$ from ALSI-PENTA (Zeolithe SN 27) were used as supports. Pt/Al_2O_3, Pt/SiO_2, Pd/Al_2O_3 and Pd/SiO_2 were prepared by incipient wetness impregnation with an aqueous $Pt(NH_3)_4(NO_3)_2$ or $Pd(NH_3)_4(NO_3)_2$ solution. The metal loading was 5.1×10^{-5} mol/g in all cases. The samples were dried in air and calcined in flowing O_2 (300 ml/min) with a heating rate 0.5 K/min, then kept at 773 K for 2 h. During reduction in 5% H_2/Ar, the temperature was increased with a ramp of 8 K/min and held at 773 K for 0.5 h. Pd/NaMFI and Pd/HMFI were obtained by ion exchange of NaMFI and HMFI with an aqueous solution (200 ml/g) of $Pd(NH_3)_4(NO_3)_2$. The diluted salt solutions were added dropwise at room temperature to the stirred slurries. Stirring was continued for 72 h, followed by filtering, washing, drying in air, calcination and reduction, as described above.

For the treatment with NH_4Cl, a reduced catalyst was contacted with 10 ml/g of an aqueous solution of, typically, 38 g/l NH_4Cl. After drying in air at room temperature,

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the metal was re-reduced in a flow of 5% H_2/Ar (8 K/min to 773 K and 30 min at 773 K). During this reduction an excess of NH_4Cl sublimed. The treatment with HCl was performed by incipient wetness impregnation of reduced M/support with HCl solution of known molarity. These samples were only dried in air and did not undergo any thermal pretreatment before mixing with Fe_2O_3.

Fe_2O_3 (hematite, J.T. Baker Chemicals, 99.5% purity) was used as supplied. Physical mixtures with a 1 : 1 mass ratio of M/support and Fe_2O_3 were prepared by grinding, using merely reduced NH_4Cl- or HCl-treated samples. When necessary, subsequent calcination of the mixtures was carried out in an O_2 flow with a heating ramp 8 K/min. Unless stated otherwise, calcination was performed up to 773 K followed by holding at 773 K for 10 min. In some cases a layered-bed arrangement of the reactor was applied with the components separated by a 2 mm porous quartz frit.

Batches of 100 g of the mixtures were characterized by temperature-programmed reduction (TPR) of Fe_2O_3 to Fe_3O_4 in a flow of 5% H_2/Ar with a flow rate of 30 ml/min and a heating ramp of 8 K/min. The hydrogen consumption was monitored by a thermoconductivity detector.

To detect the arrival of migrating species on iron oxide, an atomic resolution analytical transmission electron microscope (ARAEM) was employed. The Hitachi HF-2000 ARAEM is a cold field emission TEM equipped with an X-ray energy dispersive spectrometer (EDS). The samples were dispersed in ethanol with a low-frequency ultrasonic vibrator in a small vial. Approximately 1–2 μl of the suspension was pipetted onto a holey carbon copper grid and dried in air. The specimen was then examined in the ARAEM with 200 keV accelerating voltage.

3. Results

3.1. TPR of Fe_2O_3 mixtures with Pt/Al_2O_3, Pt/SiO_2, Pd/Al_2O_3 and Pd/SiO_2

TPR profiles of the Fe_2O_3 mixtures with reduced M/supports exhibit a single peak (see traces “without calcination” in figures 1–3), located at only slightly lower temperature (647–660 K) than that for pure Fe_2O_3 (673 K). Calcination has a profound effect on the TPR profiles of mixtures with supported platinum, as evident from a new peak appearing at 525–540 K. This observation is similar to that reported previously for mixtures of Pt/zeolite with Fe_2O_3. Its cause has been identified as migration of platinum oxide from the support onto iron oxide. This migration appears to be slower for Pt/SiO_2 and especially Pt/Al_2O_3 than for Pt/zeolites with the same Pt loading. In the latter cases, calcination of the mixtures for 10 min sufficed to completely shift the TPR peak [9]. It is obvious from figure 2 that in the mixture with Pt/Al_2O_3, even after calcination for 1 h, a significant portion of the iron oxide is reduced only at high temperature. Very little reduction enhancement is observed with Pd-containing mixtures (figure 3). Only one TPR peak is present, shifted slightly in comparison to pure Fe_2O_3. This shift is more obvious for Pd/Al_2O_3 than for Pt/SiO_2.

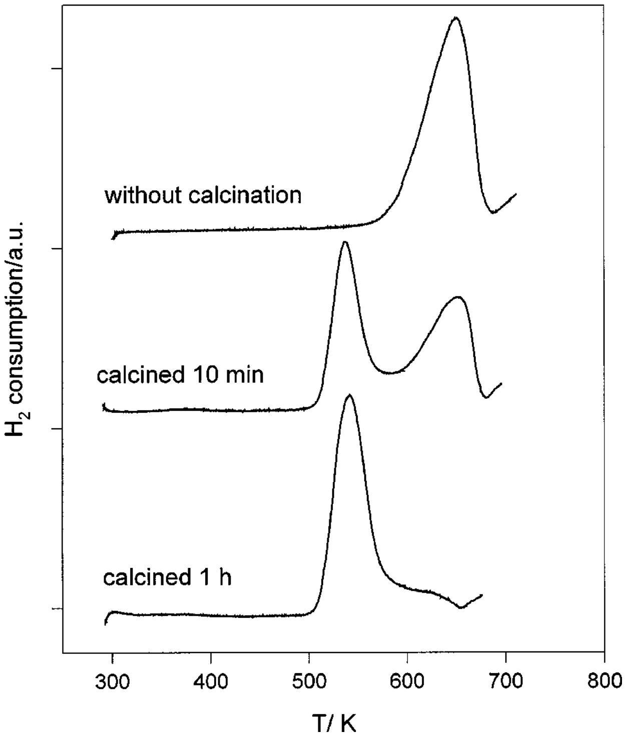

Figure 1. Effect of calcination on TPR profile of Fe_2O_3 in a mixture with reduced Pt/SiO_2.

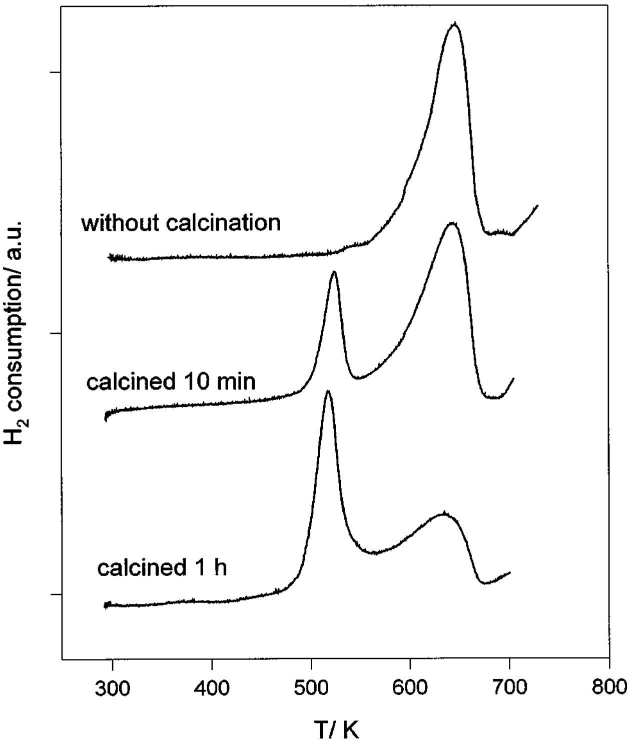

Figure 2. Effect of calcination on TPR profile of Fe_2O_3 in a mixture with reduced Pt/Al_2O_3.

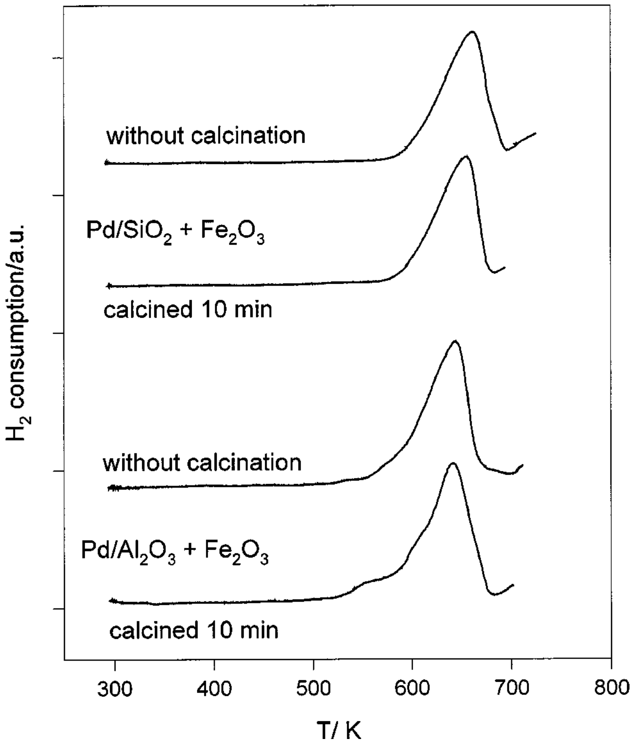

Figure 3. Effect of calcination on TPR profiles of Fe_2O_3 in mixtures with reduced Pd/SiO_2 and Pd/Al_2O_3.

3.2. Effect of NH_4Cl pretreatment of M/support on TPR profiles of mixtures with Fe_2O_3

Pretreatment of Fe_2O_3 with NH_4Cl causes an upward shift of the TPR peak of Fe_2O_3 by about 45 K (figure 4). This effect will henceforth be referred to as the *negative effect*. It is also observed for mixtures with Pt/Al_2O_3 or Pd/Al_2O_3 when these solids were treated with NH_4Cl prior to mixing with Fe_2O_3 (figure 4). The TPR profile looks the same regardless of whether the mixture was only ground or heated in argon up to 773 K (figure 4). In contrast, with SiO_2-supported Pt or Pd, a pretreatment of the supported metal with NH_4Cl, prior to its mixing with Fe_2O_3, does not lead to a shift of the TPR peak, i.e., NH_4Cl treatment of the SiO_2-supported metal causes neither a retardation nor an enhancement of the reduction.

However, dramatic changes of the TPR profiles are observed when a mixture of Fe_2O_3 with NH_4Cl-pretreated M/Al_2O_3 is calcined. As figure 5 shows, a TPR peak at low temperature is observed both with Pt/Al_2O_3 and Pd/Al_2O_3. The intensity of this peak depends on the NH_4Cl concentration during the pretreatment. With 38 g/l, the Fe_2O_3 is completely reduced at 570 K; with lower concentration of pretreatment solution the enhanced reduction is not completed. The second important condition is intimate mixing of the components. In a layered-bed experiment, in which NH_4Cl-pretreated Pt/Al_2O_3 was placed upstream to Fe_2O_3, no enhanced reduction was observed, and only a negative effect of chloride ions on Fe_2O_3 reduction was detected.

To verify the role of chloride concentration, special experiments were carried out with reduced Pd/Al_2O_3, impreg-

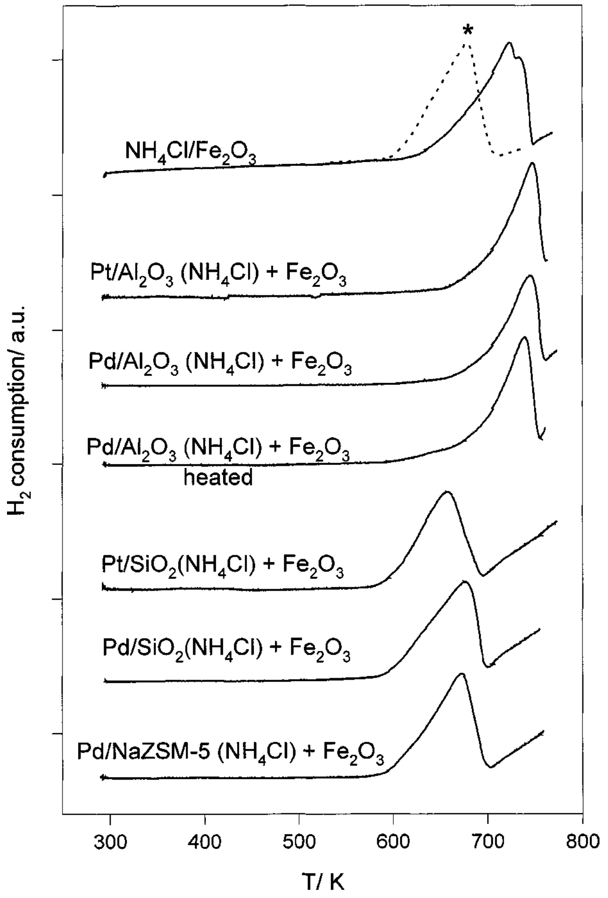

Figure 4. TPR profiles of Fe_2O_3 in mixtures with various reduced and NH_4Cl-treated samples. (∗) Peak position of pure Fe_2O_3.

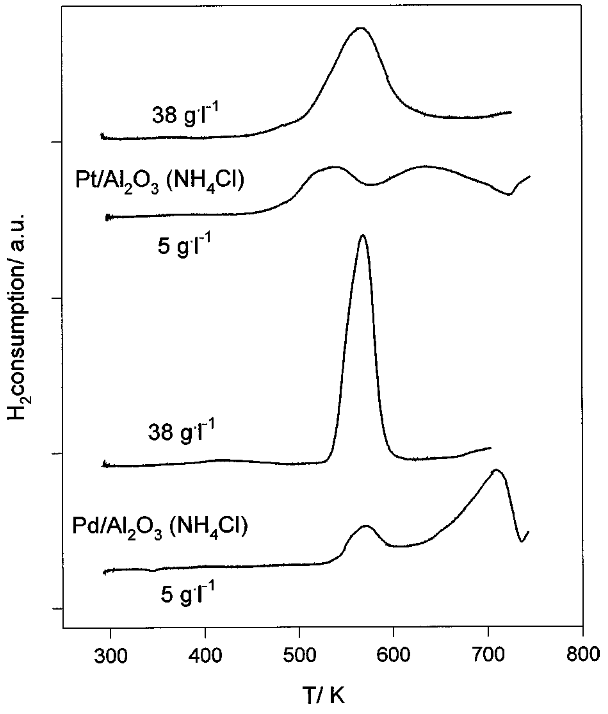

Figure 5. Effect of pretreatment with NH_4Cl solution of different concentrations on Al_2O_3-supported Pt and Pd: TPR profiles of the calcined mixtures with Fe_2O_3.

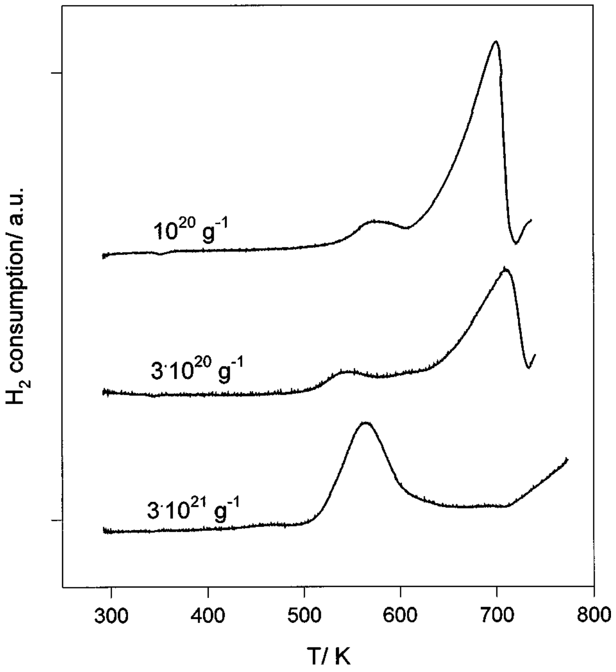

Figure 6. Effect of pretreatment of Pd/Al_2O_3 with HCl of different concentration on TPR profiles of the mixtures with Fe_2O_3. Initial chloride content in each sample is shown in the figure.

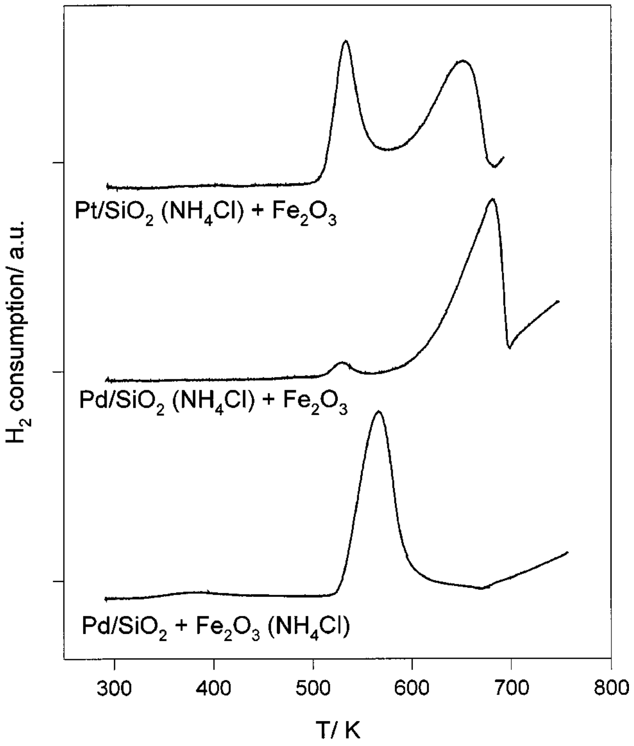

Figure 7. TPR profiles of calcined Fe_2O_3 mixtures with SiO_2-supported samples pretreated with NH_4Cl (38 g/l).

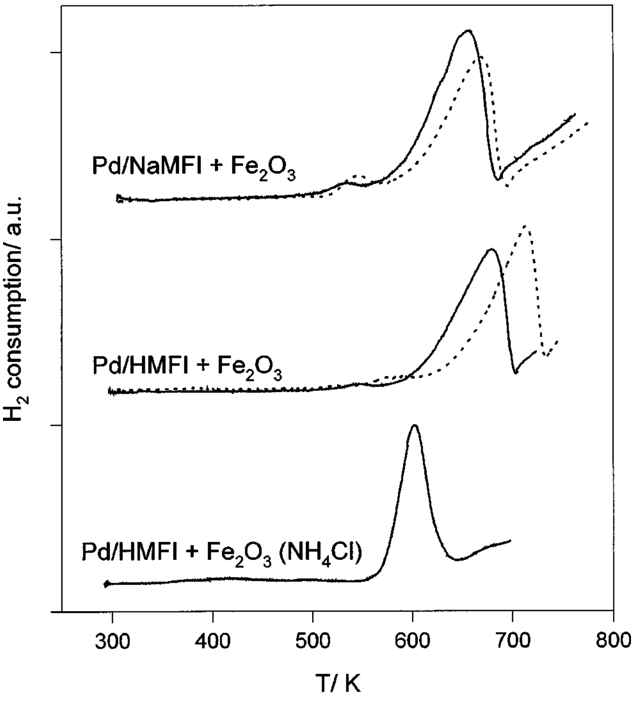

Figure 8. TPR profiles of calcined Fe_2O_3 mixtures with Pd/zeolites: untreated (- - -) and pretreated with NH_4Cl, 38 g/l (—).

nated with HCl of known molarity. After impregnating the reduced samples they were dried, mixed with Fe_2O_3, and ground without any thermal treatment in order to avoid a premature loss of volatile compounds. The mixtures were then calcined and tested with TPR following the standard procedure. The results shown in figure 6 confirm that a high initial chloride content is a prerequisite for the fully enhanced reduction of Fe_2O_3.

The same treatment had little effect on the reducibility when Pt or Pd were present on an SiO_2 support. In this case the TPR profiles of the calcined mixtures show little difference between untreated and NH_4Cl-treated M/SiO_2 (compare figures 2, 3 and 7). Likewise for Pd on a zeolite support, treatment with NH_4Cl has only minor consequences for the TPR of Fe_2O_3 in calcined mixtures (figure 8). However, if the Fe_2O_3 was first treated with NH_4Cl and subsequently mixed with untreated Pd/SiO_2 or Pd/MFI, a remarkable reduction enhancement by Pd was observed (figures 7 and 8, lower profiles).

3.3. TPR and EDS evidences of Pd and Fe migration

Among the systems studied, the mixture $Pd/SiO_2 + Fe_2O_3$ appeared to be the most illustrative for a detailed investigation of the effect of chlorides, since only very little reduction enhancement is observed in the absence of chlorides.

After testing by TPR, the mixture of Pd/SiO_2 with NH_4Cl-pretreated Fe_2O_3 (further called $Fe_2O_3(NH_4Cl)$) as described above, this mixture was examined by EDS-TEM. The TEM micrograph (figure 9) shows small dark specks on the surface of the easily recognizable Fe_2O_3 particles. An EDS analysis, performed by focusing the beam on these features, clearly reveals the presence of Pd on the Fe_2O_3 (figure 9). No such Pd-carrying Fe_2O_3 particles were found in reduced $Pd/SiO_2 + Fe_2O_3$ mixtures that had not been treated with chloride.

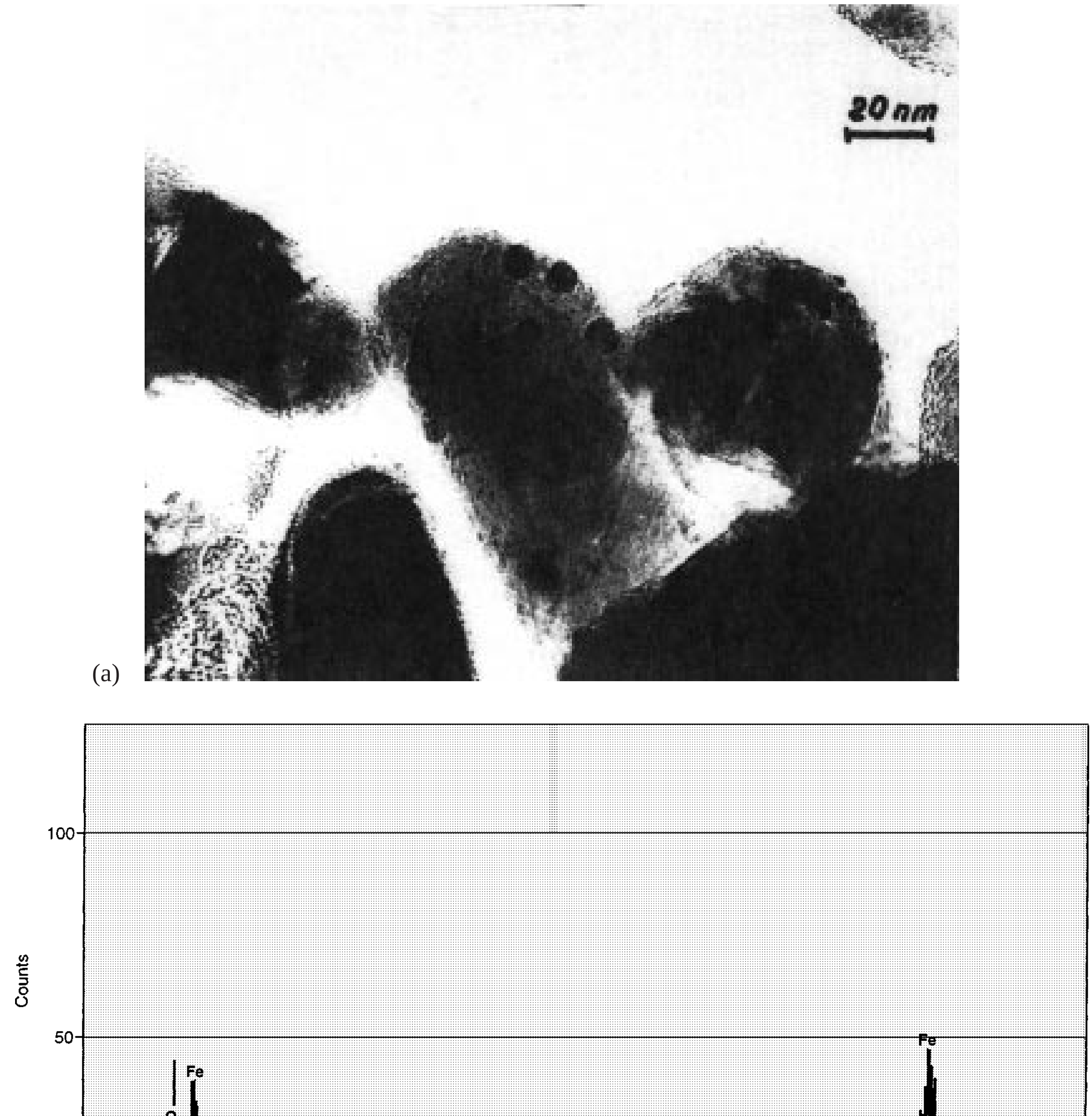

Figure 9. TEM micrograph of iron oxide particle (a) and EDS spectrum obtained in the indicated area (b).

Whereas the TPR profile of Pd is hardly visible in figure 7, figure 10 shows the profile of Pd in Pd/SiO_2. Previously we reported that the TPR of palladium displays a negative peak caused by hydrogen released upon decomposition of palladium hydride. This negative peak is absent in the TPR profiles of Pd alloys that are unable to form hydrides [10]. In the present work, TPR profiles with this typical peak are registered with the calcined mixtures Pd/SiO_2 + Fe_2O_3 and Pd/Al_2O_3 + Fe_2O_3. However, this peak is either absent or very weak for Pd/SiO_2 + Fe_2O_3(NH_4Cl) and all other mixtures for which the reduction of Fe_2O_3 had been strongly enhanced by the action of Pd. This holds in particular for mixtures of supported Pd with Fe_2O_3(NH_4Cl) (see figure 10). It follows that in these systems a palladium alloy has been formed.

In order to discriminate between transport of volatile chlorides through the gas phase and surface migration, some experiments were performed with layered beds, separated by a quartz frit. When Fe_2O_3(NH_4Cl) was placed upstream to Pd/SiO_2 during standard calcination, the presence of iron in the Pd/SiO_2 layer was detected by EDS. As this result suggests that $FeCl_3$ was transported by sublimation through

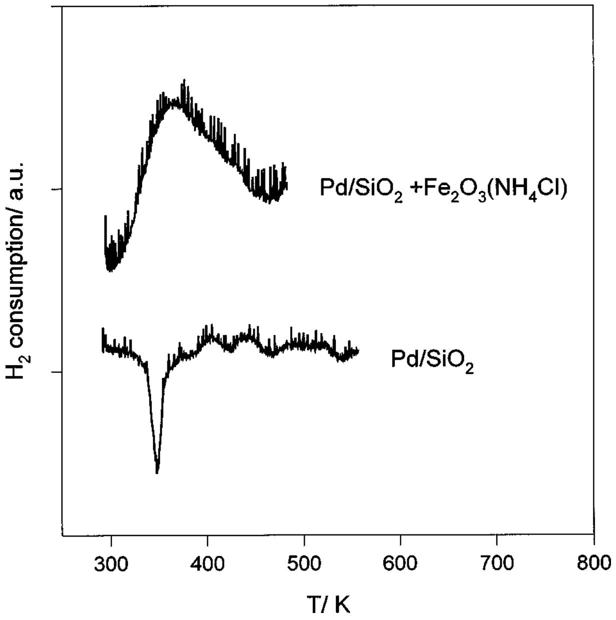

Figure 10. TPR profiles of Pd.

the gas phase and the frit, a separate experiment was carried out to confirm that chlorine had been transported: in this, a layer of untreated Fe_2O_3 was positioned downstream to $Fe_2O_3(NH_4Cl)$. After the standard calcination procedure this second layer was transferred to another reactor and subjected to TPR. Indeed the "negative effect" of retarded Fe_2O_3 reduction was observed. The same result was found when the upstream layer consisted of a mixture of $Fe_2O_3(NH_4Cl)$ + Pd/SiO$_2$. The results leave little doubt that partial chlorination of Fe_2O_3 leads to formation of volatile $FeCl_3$ (or some oxychloride) that is transported with the gas flow.

4. Discussion

Previous work of this group demonstrated, and present results confirm, that under the conditions specified in section 1 no detectable hydrogen spillover takes place from Pt or Pd on electrically insulating supports, such as SiO_2, Al_2O_3 or a zeolite, and that any migration of reduced metals across the phase boundary between support and iron oxide remains undetectable at the temperatures used here ($T \leqslant 770$ K). Enhanced reduction of Fe_2O_3 in mixtures with supported Pt or Pd is observed only after calcination in O_2. The large differences in reduction enhancement between Pt and Pd have been attributed to different surface mobilities of their oxides: PtO_2 (melting point 723 K [11]), is very mobile, but PdO (1143 K) displays little surface mobility.

The present work shows that treatment of a supported system with NH_4Cl does not facilitate the migration of Pt^0 or Pd^0 particles across a phase boundary: no enhanced Fe_2O_3 reduction has been found in mixtures with reduced metals. Instead, the TPR profiles display a retardation of Fe_2O_3 reduction in mixtures with NH_4Cl-treated Al_2O_3 carrying such metals. This indicates that chlorinated alumina interacts with iron oxide, either during the grinding process, or, more likely, upon TPR. Among the three supports studied here, only alumina is capable of retaining substantial amounts of chloride ions, whereas the silica- and zeolite-supported samples lose all NH_4Cl by sublimation.

This ability of Al_2O_3 to retain chloride ions is *one* contributing cause for the strong reduction enhancement in calcined mixtures with Al_2O_3-supported Pt and Pd. The TPR profiles of calcined mixtures of Fe_2O_3 with NH_4Cl-treated Pt/SiO$_2$, Pd/SiO$_2$ or Pd/zeolite are similar to those of the untreated samples (figures 1, 3, 7 and 8).

Once alumina, carrying substantial amounts of chloride ions at its surface, comes into contact with iron oxide, chloride ions will migrate to the Fe_2O_3. The thermodynamic driving force for this process is illustrated by the reaction enthalpy of the fictitious reaction

$$2AlCl_3 + Fe_2O_3 \rightleftharpoons 2FeCl_3 + Al_2O_3$$
$$\Delta H^0 = -170.7 \text{ kJ/mol}$$

The present data suggest that the role of the chlorinated alumina in the reduction enhancement by Pt or Pd is mainly to deliver chloride ions to the Fe_2O_3 so that volatile $FeCl_3$ is formed. Iron chloride is crucial for the observed reduction enhancement by Pt or Pd, though its formation from migrating $AlCl_3$ is only one of several possible routes. Direct impregnation of Fe_2O_3 with NH_4Cl, followed by its decomposition (see figures 7 and 8) is a valid alternative.

How, then, does iron chloride enhance the mobility of Pt or Pd precursors, so that they can leave their original support and migrate to the surface of hematite particles? No definite answer can be given at present. One possibility is that $FeCl_3$ creates chlorinated Pt or Pd complexes, comparable to hexachloroplatinate or platinum oxychloride. Such complexes are often assumed to migrate in metal redispersion when platforming catalysts are regenerated. To create $FeCl_3$ from Cl$^-$ ions on Al_2O_3, the surface concentration of Cl must be high. When Cl was deposited on Pd/Al_2O_3 by using aqueous HCl or impregnating and decomposing NH_4Cl, a Cl/Pd ratio of 100/1 was required to shift the entire TPR peak to the value typical for Fe_2O_3 decorated with Pt or Pd. It is conceivable that isolated Cl$^-$ ions will not migrate across phase boundaries on Al_2O_3, but that when a monolayer is formed, $AlCl_3$, known as a volatile though unstable compound, could migrate. Thus the multistep mechanism to chlorinate Pd or Pt via chlorinated alumina, chlorinated hematite and gas phase transport of $FeCl_3$ requires a large excess of surface Cl$^-$ in the first step. $FeCl_3$, unlike NH_4Cl, HCl or of converting Pt^0 and Pd^0 to their chlorides. This compound, therefore, is superior to others in efficiently mobilizing Pt and Pd for surface migration.

Mobile chlorinated species of Pt or Pd could include mononuclear compounds, such as chlorides, oxychlorides, hexachloroplatinate or tetrachloropalladate anion complexes, or binuclear complexes that also contain iron ions. In the absence of such binary compounds, the low melting point (661 K) of the $PdCl_2/FeCl_3$ eutectic mixture with $\sim$5% $PdCl_2$ suggests high mobility over a solid surface [12].

It is interesting that the TPR profile of Pd in figure 10 shows that all Pd is alloyed with Fe. Any unalloyed Pd should have given the usual hydride decomposition peak, but within experimental error, such a peak is absent for mixtures of Pd/SiO_2 or Pd/Al_2O_3 with Fe_2O_3 that were treated with NH_4Cl. Formation of a PdFe alloy is not unexpected for the fraction of the Pd that has migrated to the Fe_2O_3. The finding that all Pd has been alloyed leaves two possibilities: *either* all Pd has migrated to the Fe_2O_3, *or* the fraction of the Pd which is left behind on the SiO_2 surface has chemically reacted with $FeCl_3$. The first possibility implies that the surface of Fe_2O_3 is a thermodynamic sink for the migrating Pd chloride; the second would admit a statistical distribution of the Pd over both surfaces. Both possibilities have in common that interaction of subliming $FeCl_3$ with the supported metal must be a very efficient process.

5. Conclusions

Alumina, unlike silica or zeolites, is capable of retaining chloride ions from previous exposure to NH_4Cl. Chloride ions that reach the surface of Fe_2O_3 retard the reduction of that oxide in mixtures with NH_4Cl-treated and reduced Pt/Al_2O_3 and Pd/Al_2O_3.

After calcination in O_2 at 1 bar and 773 K, mixtures of NH_4Cl-treated Pt/Al_2O_3 and Pd/Al_2O_3 with Fe_2O_3 display a rather dramatic reduction enhancement of the Fe_2O_3. This effect increases with the NH_4Cl concentration of the aqueous solution used to treat the Pt/Al_2O_3 or Pd/Al_2O_3 prior to mixing and calcination. Treatment with aqueous HCl causes the same effect and shows a similar concentration dependence. No such effect is observed with SiO_2- or zeolite-supported metals unless iron oxide itself is pretreated with NH_4Cl.

The reduction enhancement is assumed to result from the formation of a volatile chlorinated iron compound, presumably iron trichloride, which is formed when iron oxide interacts with Al_2O_3 that is covered by Cl^- ions. The iron chloride participates in the transport of Pt or Pt species across the phase boundary. Once Pt or Pd precursors on iron oxide are reduced to the metals, they give rise to thermodynamically permitted hydrogen spillover. In the case of Pd, the reduced metal is identified as an alloy with iron, indicating that interaction of $FeCl_3$ with Pd is a very efficient process.

Acknowledgement

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