# Reduction enhancement of $Fe_2O_3$ in physical mixtures with Pt/mordenite *via* Pt migration or 'hydrogen spillover'

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Mixing Fe<sub>2</sub>O<sub>3</sub> with Pt/NaMor of similar grain size, followed by grinding in a mortar and calcination in O<sub>2</sub>, leads to a remarkable enhancement of the reducibility of the  $Fe_2O_3$  with hydrogen. The TPR profile of such mixtures is virtually identical with that of  $Fe_2O_3$  onto which Pt was deposited chemically. It is concluded that in the ground and calcined mixtures Pt migration from the zeolite to the iron oxide is crucial. Upon varying the amount of deposited Pt in Pt/Fe<sub>2</sub>O<sub>3</sub> between 0.001% and 1%, TPR profiles are obtained showing two discrete peaks characterizing a Pt promoted and an unpromoted reduction of Fe<sub>2</sub>O<sub>3</sub> respectively. No Pt migration occurs in mixtures of prereduced Pt/NaMor with Fe<sub>2</sub>O<sub>3</sub>; this shows that surface migration of Pt<sup>0</sup> clusters is negligible, but transport of PtO<sub>2</sub> either through the gas phase or via the surface is likely. Pt migration is also detectable at room temperature in mixtures stored for weeks in a moist atmosphere; in this case the data suggest surface migration of hydrated  $Pt^{2+}$  ions; the TPR profiles are distinctly different from those of the mixtures calcined in O<sub>2</sub>. TPR also permits discrimination between the promotion of oxide reduction by migrating Pt and 'true' hydrogen spillover. The latter phenomenon requires transport of H atoms via protons and electrons and is realized with powder mixtures containing a semiconducting oxide, such as TiO<sub>2</sub>. Its TPR signature is a broad peak located between those for unpromoted and Pt promoted reduction. Physical mixtures of Fe<sub>2</sub>O<sub>3</sub> and Pt/NaMor catalyze the reduction of acetic acid vapor to acetaldehyde via a Mars-van Krevelen mechanism. In this case Pt migration helps to regenerate oxygen vacancies in the  $Fe_3O_4$  surface, whereas direct contact of  $CH_3CO_2H$ vapor with Pt results in the formation of methane and higher hydrocarbons. The promoting effect of Pt is not observed after prereduction of Pt/NaMor, because Pt<sup>0</sup> does not migrate effectively under the conditions used.

Many catalytic and solid state reactions require surface transport of intermediates across phase boundaries. For instance, the reduction of an oxide such as  $WO_3$  or  $Fe_2O_3$  with hydrogen is significantly accelerated by the presence of Pt particles that are deposited on the oxide. For such systems it is generally assumed that  $H_2$  is dissociatively chemisorbed on the Pt surface, H atoms subsequently cross the phase boundary between Pt and the oxide and attach themselves to  $O^{2^-}$  ions, while an electron is added to the transition metal cation:

$$H_{ads} + O^{2-} - M^{n+} \rightarrow H^+ - O^{2-} - M^{(n-1)+}$$
 (1)

Early observations of this phenomenon were reported by Sinfelt and Lucchesi,<sup>1</sup> Khoobiar<sup>2</sup> and Kuriacose.<sup>3</sup> Boudart introduced the term 'hydrogen spillover'<sup>4</sup> which is now generally used. The literature on this subject is reviewed in several papers.<sup>5–7</sup>

This simple scheme breaks down, however, when the source of the H atoms and the reducible oxide are separated by a material characterized by (i) strongly endothermic adsorption of hydrogen atoms and (ii) negligible semiconductivity.

Materials for which these criteria are valid include SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and zeolites. The first criterion prevents transport of H atoms as chemisorbed but mobile  $H_{ads}$ , because their surface concentration is prohibitively low at low temperature. An alternative path transports H atoms *via* protons and electrons. Indeed, the mobility of protons is high over surfaces exposing both O<sup>2-</sup> ions and OH<sup>-</sup> groups, but the transport of electrons requires semiconductivity which can be translated, for pure oxides, as thermodynamic coexistence of cations in two valence states M<sup>n+</sup> and M<sup>(n-1)+</sup>. In the absence of impurities, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and zeolites are thought to be electric insulators; consequently the second criterion seems to exclude them from the group of prospective candidates for hydrogen spillover at low temperature.

Still, there is a large amount of literature evidence showing that chemical reduction processes are often accelerated by the presence of a metal such a platinum or nickel, even if this metal or its precursors is separated from the reducible oxide by materials for which criteria (i) and (ii) appear to apply.<sup>8-12</sup> Although the term hydrogen spillover is often used to describe the observed acceleration of oxide reduction, this term is not always justified and a better definition of the migrating species appears desirable. In a previous study we showed that the reduction of sulfate groups on zirconia is markedly enhanced when this material is present in a physical mixture with zeolite supported Pt clusters, but there remained uncertainty to what extent this phenomenon could be ascribed to true spillover in the rigorous definition given above.13 We have also shown that reduction of metal ions in zeolite cavities is enhanced by the presence of ions of a second, more easily reducible metal,<sup>14-16</sup> but the precise nature of the atomic steps has not yet been unravelled.

In some cases, clear evidence exists that the migrating species is actually the transition metal (TM) or its precursor. For instance, work of this group showed that co-reduction of  $Al_2O_3$  supported Re-oxide and Pt-oxide is entirely controlled by the surface mobility of the TM ions. If they are immobile, TPR gives two separate peaks, one for Pt at low and one for Re at higher temperature. However, if both ions can migrate over the surface, only one TPR peak is observed, and is located at low temperature. In this case, and only in this case, are the reduced particles identified as PtRe alloy clusters.<sup>17</sup>

Recently, hydrogen spillover was assumed by Pestman *et al.*<sup>18,19</sup> to be crucial for the catalytic reduction of acetic acid to acetaldehyde over physical mixtures of, for instance, unsupported  $Fe_2O_3$  and  $SiO_2$  supported platinum. In this case, spiltover H atoms are assumed to partially reduce the surface of the iron oxide; the acetic acid molecules re-oxidize it, in a Mars-van Krevelen mechanism, by depositing one of its oxygen atoms into an oxide vacancy:

$$2 H_{spiltover} + O_{surface}^{2-} \rightarrow \Box_{surface} + H_2O$$
(2a)

$$CH_3CO_2H + \square_{surface} \rightarrow CH_3CHO + O_{surface}^{2-}$$
 (2b)

$$H_2 \rightarrow 2 H_{spiltover}$$
 (2c)

which adds up to:

$$CH_3CO_2H + H_2 \rightarrow CH_3CHO + H_2O$$
 (2d)

This observation potentially opens challenging perspectives for selective catalysis, as geometric arrangements are conceivable in which Pt acts exclusively as a source of hydrogen spillover, whereas the acetic acid is prevented from contacting the Pt particles directly and thus undergoing undesired reactions.

In the present work we first ascertain whether physical mixtures of the type  $Fe_2O_3 + Pt/zeolite$  have the same catalytic propensity for the selective reduction of acetic acid to acetaldehyde as the system  $Fe_2O_3 + Pt/SiO_2$  described by Pestman *et al.*<sup>18</sup> It is further attempted to differentiate between (i) true H spillover, *i.e.* migration of H atoms over the zeolite and the iron oxide surfaces and (ii) migration of the transition metal.

In the latter case it appears desirable to identify the migrating species; are these Pt metal clusters Pt oxide clusters or Pt ions?

#### Experimental

Pt/NaMor (0.63 wt.% Pt-load; Mor = Mordenite) was prepared by ion exchange of a diluted aqueous solution of Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (Alfa Aesar) with a NaMor slurry [200 ml (g zeolite)<sup>-1</sup>]. The zeolite used was LZ-M-5 (Si : Al = 5.6) from UOP. The ion exchanged catalyst was dried in air and subsequently calcined in pure O<sub>2</sub> (flow rate: 500 ml min<sup>-1</sup>; heating rate 0.1 K min<sup>-1</sup> to 783 K). At this stage it was stored over NH<sub>4</sub>Cl solution and used for further experiments.

 $Fe_2O_3$  (hematite, J. T. Baker Chemicals; 99.5% purity) and TiO<sub>2</sub> (P25, Degussa) were used as supplied. Pt/Fe<sub>2</sub>O<sub>3</sub> and Pt/TiO<sub>2</sub> were prepared by wet impregnation of Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> with an aqueous solution of Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (Alfa Aesar) and subsequent drying in air and calcination in O<sub>2</sub> (783 K). Five samples of Pt/Fe<sub>2</sub>O<sub>3</sub> with 1%, 0.1%, 0.03%, 0.01% and 0.001% Pt-loading were prepared using consecutively diluted solutions. Pt/TiO<sub>2</sub> contained 1 wt.% Pt. Fe<sub>3</sub>O<sub>4</sub> and Pt/Fe<sub>3</sub>O<sub>4</sub> (1 wt.% Pt-loading) were synthesized by isothermal reduction of Fe<sub>2</sub>O<sub>3</sub> and Pt/Fe<sub>2</sub>O<sub>3</sub> in H<sub>2</sub> at 623 K and 573 K, respectively.

The used  $Fe_2O_3$  has a BET surface of 8.1 m<sup>2</sup> g<sup>-1</sup>, which leads to an average particle size of 140 nm. The size distribution of  $Fe_2O_3$  crystallites observed by TEM were 50 nm to 250 nm, which is in good agreement with the value obtained from BET. It follows that microporosity can be neglected for these particles. However, crystallites will agglomerate to form larger particles of 1–2 µm diameter with mesopores.

Experiments were done using either one component catalysts or physical mixtures of two or three components. The two component mixtures were prepared by mixing and thoroughly grinding amounts of equal weight. When desired, a third component was added afterwards and the entire mixture ground again.

The catalytic studies were carried out in a standard plugflow microreactor, comprising a gas supply with an impurity trap, a saturator to admit liquid, a temperature controlled plug-flow microreactor and a two column gas chromatograph (50 m HP-PONA capillary column with FID; Alltech-Chemipack C18 packed column with TCD). The feed gas of H<sub>2</sub> (60 ml min<sup>-1</sup>) contained 20–25 mbar CH<sub>3</sub>CO<sub>2</sub>H after saturation. The amount of catalyst was 200 mg if using a single component and 400 mg in the case of physical mixtures. The reaction was studied in a temperature programmed way. After an initial treatment at 473 K for 30 min in H<sub>2</sub> and 30 min in the reaction mixture the temperature was increased with a ramp of 1 K min<sup>-1</sup> up to 723 K. During this treatment,  $Fe_2O_3$  was reduced to  $Fe_2O_4$ , the actual catalyst as shown by Pestman *et al.*<sup>18</sup> Subsequently, the temperature was decreased with the same ramp to 473 K. The reaction profile was recorded during the entire temperature cycle.

The kinetics of  $Fe_2O_3$  reduction with a 5%  $H_2$  in Ar gas mixture was studied as a temperature programmed reduction (TPR) profile with a flow rate of 30 ml min<sup>-1</sup> and a temperature ramp of 8 K min<sup>-1</sup>. The hydrogen uptake was monitored by a thermal conductivity detector. In the mixtures the content of  $Fe_2O_3$  was always kept constant at 50 mg, while the total amount of the sample varied. Since the pretreatment of the samples is an important issue in this research, these conditions will be specified when the results are presented.

For transmission electron microscopy (TEM) of the samples, a Hitachi HF-2000 analytic electron microscope operated with 200 keV and equipped with an energy dispersive X-ray (EDX) analyser was used.

#### Results

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# Effect of platinum on $Fe_3O_4$ in the selective reduction of acetic acid

In Fig. 1 the catalytic reduction of acetic acid is compared for  $Fe_3O_4$  and  $Pt/Fe_3O_4$  as the catalyst. The partial pressures of acetic acid and the reaction products are plotted vs. temperature. Over  $Fe_3O_4$  [Fig. 1(a)] the main products at high temperature are hydrocarbons, especially methane, and carbon monoxide. Acetaldehyde is produced with a selectivity of only 20% at a maximum which is reached at 670 K. Impregnation of  $Fe_3O_4$  with Pt [Fig. 1(b)] leads to an overall increase in activity and also an increase in selectivity towards acetaldehyde. Additionally, the formation of ethanol is

**Fig. 1** Catalytic conversion of acetic acid vapor: ( $\blacksquare$ ) CH<sub>3</sub>CO<sub>2</sub>H, ( $\blacklozenge$ ) CH<sub>3</sub>CHO, ( $\blacklozenge$ ) CH<sub>3</sub>CH<sub>2</sub>OH, ( $\bigcirc$ ) CH<sub>4</sub>, ( $\bigtriangleup$ ) CO, ( $\bigtriangledown$ ) C<sub>2+</sub>. (a) Catalyst: unsupported Fe<sub>2</sub>O<sub>3</sub>; (b) catalyst: Pt/Fe<sub>2</sub>O<sub>3</sub> produced by Pt impregnation onto Fe<sub>2</sub>O<sub>3</sub>.



observed. These results confirm the earlier observations of Pestman et al.<sup>18</sup>

In a second experiment, a physical mixture of  $Fe_3O_4$  with Pt/NaMor was probed as the catalyst. It is seen from Fig. 2(a) that the conversion of acetic acid at low temperature is significantly higher than with  $Fe_3O_4$  or  $Fe_3O_4$  impregnated with Pt. Acetaldehyde is a major product, its yield peaks at 600 K. Above 650 K the predominant reaction products are CO and methane, other hydrocarbons are also formed. Fig. 2(b) shows the reaction profile for Pt/NaMor. Over this catalyst, methane, CO and small amounts of higher hydrocarbons are the only products. It is evident that the catalytic profile over the mixture of  $Fe_3O_4$  and Pt/NaMor is not a superposition of the profiles over the single components. A significant interaction between the two components has to be considered. Understanding the nature of this interaction will be the main objective of the research described below.

#### TPR profiles of Fe<sub>2</sub>O<sub>3</sub> : the effect of added platinum

If some chemical interaction between Pt in Pt/NaMor and the iron oxide is responsible for the non-additive behavior of that mixture in the catalytic test, such interaction should also be instrumental in the reduction of the Fe<sub>2</sub>O<sub>3</sub> with H<sub>2</sub> to Fe<sub>3</sub>O<sub>4</sub>. In general, a mere reduction is less complicated than a catalytic network that includes other steps than local reduction of the catalyzing oxide. Reduction of Fe<sub>2</sub>O<sub>3</sub> starts at the surface of this solid and requires sites where H<sub>2</sub> molecules can dissociate. Platinum might be helpful in this step, if it is in direct physical contact, so that classical spillover to the oxide is possible. This propensity was already shown for Pd/Fe<sub>2</sub>O<sub>3</sub>.<sup>20</sup> Whether Pt clusters that are encaged inside an insulating material, such as mordenite, can exert an effect on the reduction of Fe<sub>2</sub>O<sub>3</sub> is not obvious *a priori*.



**Fig. 2** Catalytic conversion of acetic acid vapor: ( $\blacksquare$ ) CH<sub>3</sub>CO<sub>2</sub>H, ( $\blacklozenge$ ) CH<sub>3</sub>CHO, ( $\blacklozenge$ ) CH<sub>3</sub>CH<sub>2</sub>OH, ( $\bigcirc$ ) CH<sub>4</sub>, ( $\bigtriangleup$ ) CO, ( $\bigtriangledown$ ) C<sub>2+</sub>. (a) Catalyst: physical mixture of Fe<sub>2</sub>O<sub>3</sub> + Pt/NaMor; (b) catalyst: Pt/NaMor.



Fig. 3 TPR profiles of  $Fe_2O_3$  reduction to  $Fe_3O_4$ . Curve A: pure  $Fe_2O_3$ ; curve B:  $Pt/Fe_2O_3$  with 1 wt.% Pt deposited by impregnation.

At first, the reduction behavior of pure  $Fe_2O_3$  under TPR conditions was studied. The profile (Fig. 3 curve A) shows an asymmetric reduction signal with a maximum at 670 K. In this and the following TPR experiments the area under this reduction peak corresponds within 10% error to the hydrogen consumption for the reaction:

$$3 \text{ Fe}_2 \text{O}_3 + \text{H}_2 \rightarrow 2 \text{ Fe}_3 \text{O}_4 + \text{H}_2 \text{O}$$
 (3)

The increasing hydrogen consumption above 700 K indicates further reduction to  $Fe_xO$  and  $Fe^0$ . This reduction behavior of  $Fe_2O_3$  was observed several times before.<sup>20,21</sup> In curve B of Fig. 3 the reduction profile of impregnated 1% Pt/Fe<sub>2</sub>O<sub>3</sub> is presented. The presence of Pt at the surface leads to a marked lowering of the temperature of the maximum in the reduction profile to 560 K. This indicates that the ability of metallic Pt to dissociatively adsorb hydrogen is helpful; as both solids are in direct physical contact the result can be explained in terms of the classical hydrogen spillover model.

Fig. 4 shows reduction experiments of physical mixtures of  $Fe_2O_3$  with Pt/NaMor. Curve A represents the profile of a freshly prepared mixture with no further initial pretreatment. In this mixture the Pt inside the zeolite is in its oxidized state,



**Fig. 4** TPR profiles of physical mixtures of  $Fe_2O_3$  with Pt/NaMor. Curve A: freshly ground mixture; curve B: mixture after calcination on  $O_2$  at 673 K for 10 min; curve C: physical mixture that was not ground but merely shaken; curve D: mixture after storage for several weeks.

as the Pt/NaMor had been calcined to 783 K in pure  $O_2$ . The physical mixture is reduced under the same TPR conditions as the samples mentioned above. A very small signal indicating the reduction of Pt is hardly visible because of the very low Pt loading. Profile A shows two reduction peaks of Fe<sub>2</sub>O<sub>3</sub> at 550 K and 660 K. The second peak, which corresponds nicely to the signal of pure Fe<sub>2</sub>O<sub>3</sub> in Fig. 3, curve A, is much more prominent than the first one, indicating that the majority of Fe<sub>2</sub>O<sub>3</sub> does not take any kinetic advantage of the presence of Pt inside the zeolite.

This situation changes completely when the physical mixture is calcined in pure  $O_2$  at 673 K for 10 min prior to the TPR run, as can be seen in Fig. 4, curve B. Here, the most prominent peak is the low temperature reduction signal with its maximum at 560 K corresponding to curve B in Fig. 3. Only a tiny signal remains at 660 K. Now the system behaves like Pt in direct contact with Fe<sub>2</sub>O<sub>3</sub>.

To clarify the effect of the grinding procedure during preparation of the physical mixture, the next experiment was carried out after gentle mixing of the sample. The components were ground separately and mixed inside the reactor by merely shaking it for 5 min. This mixture was calcined in  $O_2$ in the same way as described above. Curve C in Fig. 4 shows its TPR profile. Clearly, the main reduction takes place at high temperatures (660 K), only a small reduction signal is visible at 550 K. It follows that calcining in O<sub>2</sub> at 673 K though necessary, is not sufficient to develop the strong reducibility enhancement that was manifest in curve B. As gently shaking will lead to less intimate contact between the two components, and on average a much lower contact area will be established, this experiment indicates that close proximity between Fe<sub>2</sub>O<sub>3</sub> and Pt/NaMor is essential for the Pt induced reduction enhancement. Therefore all further samples with physical mixtures were prepared by grinding.

The most surprising observation was made when a physical mixture was examined which had been stored after mixing for several weeks at room temperature under atmosphere. The TPR of this sample was recorded without previous calcination; the result is presented in curve D of Fig. 4. Here, the profile shows two maxima at 560 K (sharp) and at 610 K (broad). Comparing this to the initial state immediately after mixing (Fig. 4, curve A) indicates that even at room temperature an interaction between the two components takes place when they are in close contact. Since this interaction is not immediately observable after mixing, a slow chemical reaction has to be considered. One possibility is the migration of Pt ions or Pt-oxide clusters out of the zeolite onto the iron oxide. This is, indeed, strongly suggested by the identical reduction profile of the mixture after calcination (Fig. 4, curve B) and the  $Pt/Fe_2O_3$  sample (Fig. 3, curve B) where Pt had been deposited onto  $Fe_2O_3$ .

To detect a possible Pt migration onto iron oxide, TEM studies with EDX were performed, however, no evidence was found for the presence of Pt on  $Fe_2O_3$ . If Pt has indeed migrated out of the zeolite onto the iron oxide, its presence there is below the detection limit of these methods.

#### Effect of the amount of platinum in Pt/Fe<sub>2</sub>O<sub>3</sub>

To get an idea as to the amount of Pt necessary to give enhanced reduction of  $Fe_2O_3$ , a series of impregnated Pt/Fe<sub>2</sub>O<sub>3</sub> samples were prepared, having Pt contents of 1 wt.%, 0.1 wt.%, 0.03 wt.%, 0.01 wt.% and 0.001 wt.%, respectively. The TPR profiles of these five samples are shown in Fig. 5A–E. It is obvious that there are two distinct reduction domains, those which are influenced by the presence of platinum at the surface (540–560 K) and those which are not (650– 660 K). Remarkably, there is no intermediate reduction domain. Reduction is either enhanced by Pt and then gives a TPR peak at 550 K, or it is not enhanced and the TPR peak



**Fig. 5** TPR profiles of  $Pt/Fe_2O_3$  with various amounts of Pt. Curve A: 1 wt.% Pt; curve B: 0.1 wt.% Pt; curve C: 0.03 wt.% Pt; curve D: 0.01 wt.% Pt; curve E: 0.001 wt.% Pt.

is located at 660 K. A possible model is that some fraction of the  $Fe_2O_3$  is in efficient contact with Pt, while the other fraction is not. With decreasing Pt content the former fraction decreases and the latter increases.

Even with 0.001 wt.% Pt there is still low temperature reduction visible. The reducibility of  $Fe_2O_3$  appears to be a highly sensitive phenomenon, registering even very small amounts of Pt on its surface.

#### **Diluting experiments**

Diluting a physical mixture with an inert third solid provides a statistical means to increase the average distance between the component particles. If Pt migrates only in the stage before the third component is added, one would expect that the position of the TPR signals is unaffected by the diluent. Therefore, experiments were designed in which the samples were diluted with a tenfold excess (with respect to the Fe<sub>2</sub>O<sub>3</sub> component) with NaMor. Preliminary tests indicated that if using mordenite as the third component such ternary mixtures had to be prepared in a dry atmosphere using precalcined NaMor (673 K in O<sub>2</sub>) in order to minimize the effects of physisorbed water. The first TPR profile (Fig. 6, curve A) shows the behavior of 0.1% Pt/Fe<sub>2</sub>O<sub>3</sub> diluted with NaMor. Since in this case Pt is known to be in contact with  $Pt/Fe_2O_3$ we expect the reduction signal to be near 550 K. This is confirmed by experiment, the TPR peak is located at 560 K, only 10 K higher than in the undiluted sample (Fig. 5, curve B). This small difference can be attributed to the effect of physisorbed water in NaMor or to a different temperature distribution in the reactor due to the larger volume of the sample.

In curve B of Fig. 6 the TPR profile is presented of a diluted  $Pt/NaMor + Fe_2O_3$  mixture, which was calcined in  $O_2$  at 673 K for 10 min prior to dilution. Again, the maximum of the reduction signal is at 560 K, thus only slightly higher than that of the undiluted mixture (Fig. 4, curve B). This is, again, strong evidence that during calcination in  $O_2$  some Pt migrates to  $Fe_2O_3$ . Moreover, the profiles of curve A and B are very similar, suggesting that the amount of migrated Pt is close to 0.1 wt.% with respect to  $Fe_2O_3$ .

The situation is more complicated in the case of physical mixture that had been stored for extensive periods. Curve C shows the profile of a diluted physical mixture after storage for several months. In this case the reduction signal becomes very broad, with a smooth transition into the further reduction of iron oxide. The low temperature maximum was



Fig. 6 TPR profiles of ternary mixtures  $Fe_2O_3 + Pt/NaMor + NaMor$ . Curve A: 0.1%  $Pt/Fe_2O_3 + NaMor$ ; curve B:  $Fe_2O_3 + Pt/NaMor$  calcined at 673 K prior to dilution with NaMor; curve C:  $Fe_2O_3 + Pt/NaMor$  after storage for three months prior to dilution with NaMor.

near 620 K, which is 50 K higher than for the undiluted mixtures presented in Fig. 4, curve D.

#### Effect of 'true' hydrogen spillover on TPR profiles

All results described thus far can be rationalized in terms of a model assuming migration of platinum. So far, it is not clear if also migration of hydrogen atoms plays a role as in the classical model of hydrogen spillover. Therefore the following experiments were carried out that focus on this possibility.

There is ample evidence in the literature<sup>22,23</sup> that  $TiO_2$ , a semiconducting material, has the ability to transport spiltover hydrogen atoms, *i.e.* protons and electrons. If Pt is supported on  $TiO_2$ , it can be expected that a 'true' hydrogen spillover effect should occur in physical mixtures with  $Fe_2O_3$ . The question is, how would this be manifest phenomenologically in TPR profiles? Therefore, TPR experiments were designed with physical mixtures of  $Fe_2O_3$  with Pt/TiO<sub>2</sub>.

Fig. 7, curve A shows the profile of this mixture. The main reduction peak is observed at 560 K, which corresponds exactly to that observed for  $Pt/Fe_2O_3$ . To make sure that  $TiO_2$  itself does not enhance the reduction of  $Fe_2O_3$ , a physical mixture of  $Fe_2O_3$  with pure  $TiO_2$  has been investigated. Fig. 7, curve C shows the result. Now the reduction maximum is observed at 690 K, which can be assigned to the reduction of pure  $Fe_2O_3$ , not influenced by  $TiO_2$ .

Since the Pt loading of  $TiO_2$  could be partially located on the outer surface, this could lead to a direct contact of Pt and  $Fe_2O_3$ , resulting in the behavior observed in Fig. 7, curve A. To reduce this effect, again a dilution experiment was performed where the Fe<sub>2</sub>O<sub>3</sub> and Pt/TiO<sub>2</sub> physical mixture was diluted with a tenfold excess of pure TiO<sub>2</sub>. This should lead to a statistical separation of the two interacting sites. Curve B in Fig. 7 shows the result of this experiment. As expected, the initial reduction signal at 560 K is strongly depressed. But now the main reduction signal shows its maximum to be 620 K and very broad. This is a completely new behavior. Since the diluting compound is still able to spillover hydrogen, this new reduction effect has to be assigned to the 'true' spillover of hydrogen. The shift and broadening of the signal can be explained by the larger distance over which the hydrogen must be transported.

This effect can be used as a tool to investigate other substances for their spillover abilities. In the next experiment this strategy was applied to study  $Fe_3O_4$ . Fig. 8, curve A shows



Fig. 7 TPR profiles of physical mixtures of  $Fe_2O_3 + Pt/TiO_2$ . Curve A:  $Fe_2O_3 + Pt/TiO_2$ ; curve B:  $Fe_2O_3 + Pt/TiO_2 + tenfold$  excess of  $TiO_2$ ; curve C:  $Fe_2O_3 + TiO_2$ .

the TPR profile of a physical mixture of  $Pt/Fe_3O_4$  with  $Fe_2O_3$ . Again the maximum reduction peak is observed at 540 K, due to the presence of platinum. In contrast, pure  $Fe_3O_4$  gives no enhanced reduction of  $Fe_2O_3$ , discernible by the high temperature reduction maximum at 660 K (Fig. 8, curve C).

Again, the decisive clue is obtained from the diluted mixture. Fig. 8, curve B shows the TPR profile of a physical mixture of  $Pt/Fe_2O_3$  and  $Fe_2O_3$  with a tenfold excess of pure  $Fe_3O_4$ . As already observed in the experiments with TiO<sub>2</sub> the initial reduction signal at 540 K decreases and a new signal at 610 K shows up. Since  $Fe_3O_4$  is also a semiconducting material, this can be interpreted again as the effect of hydrogen spillover.

#### Experiments with prereduced Pt/NaMor

In previous TPR experiments concerning physical mixtures of Pt/NaMor and  $Fe_2O_3$  there are indications that there is migration of Pt, whether as oxide or as ions or as metal particles, from the zeolite to the iron oxide. To examine the last possibility, the Pt/NaMor compound has to be reduced.



Fig. 8 TPR profiles of physical mixtures with  $Fe_3O_4$ . Curve A:  $Fe_2O_3 + Pt/Fe_3O_4$ ; curve B:  $Fe_2O_3 + Pt/Fe_3O_4 + tenfold$  excess  $Fe_3O_4$ ; curve C:  $Fe_2O_3 + Fe_3O_4$ .



Fig. 9 TPR profiles of physical mixtures  $Fe_2O_3 + Pt/NaMor$ . Effect of pretreatments: curve A:  $Fe_2O_3 + prereduced Pt/NaMor$ ; Curve B: same as A after calcination at 673 K for 10 min; curve C:  $Fe_2O_3 + prereduced Pt/NaMor$ , after storage for 6 weeks.

Therefore, the following TPR experiments were carried out, using physical mixtures of  $Fe_2O_3$  with prereduced (at 823 K in 5% H<sub>2</sub>-Ar) Pt/NaMor. Since the initial mixture with no further pretreatment (Fig. 4, curve A) did not show any indications of Pt migration, this is also to be expected for those mixtures containing prereduced Pt/NaMor (Fig. 9, curve A).

It becomes more interesting when the different pretreatments are applied to this mixture. Fig. 9, curve B shows the profile after calcination in  $O_2$  at 673 K for 10 min. The maximum is obtained at 540 K, indicating that there is the same behavior as after calcination of the initial mixture (Fig. 4, curve B). Since pretreatment took place in an  $O_2$  atmosphere at elevated temperature, this can be explained by reoxidation of the small Pt metal particles leading to the same behavior as observed with the initial mixture.

However, in the TPR profile of a mixture containing prereduced Pt/NaMor, which was stored for 6 weeks, the main reduction peak remains at 660 K (Fig. 9, curve C). This is a big difference to that of the initial mixture, presented in Fig. 4, curve D. This last experiment indicates clearly that the migration of Pt<sup>0</sup>-metal particles is not responsible for the effects observed at low temperature. Rather, the mixture remains unaltered when using prereduced Pt/NaMor.



**Fig. 10** Catalytic conversion of acetic acid vapor: ( $\blacksquare$ ) CH<sub>3</sub>CO<sub>2</sub>H, ( $\blacklozenge$ ) CH<sub>3</sub>CHO, ( $\blacklozenge$ ) CH<sub>3</sub>CH<sub>2</sub>OH, ( $\bigcirc$ ) CH<sub>4</sub>, ( $\triangle$ ) CO, ( $\bigtriangledown$ ) C<sub>2+</sub>. Catalyst: physical mixture of Fe<sub>2</sub>O<sub>3</sub> + prereduced Pt/NaMor.

Therefore, the catalytic behavior of a physical mixture containing prereduced Pt/NaMor and  $Fe_3O_4$  was investigated. Fig. 10 shows that the catalytic signature of this mixture is identical with that of pure  $Fe_3O_4$ ; *i.e.* in this mixture no promoting effect of Pt is detected. This result proves that the promoting effect shown in Fig. 2(a) is entirely caused by Pt which migrated, as an oxidic Pt precursor, from the zeolite onto the iron oxide.

# Discussion

This discussion will focus on the enhanced reducibility of  $Fe_2O_3$  to  $Fe_3O_4$  in physical mixtures with Pt/NaMor. It is also related to the enhanced activity and selectivity in the catalytic reduction of acetic acid to acetaldehyde on  $Fe_3O_4$ . In a superficial way, this effect might be described in terms of hydrogen spillover from Pt, located in the zeolite, to iron oxide. However, a thorough analysis of the reduction kinetics under different circumstances leads to a more differentiated point of view.

First, the temperature of maximum reduction rate of  $Fe_2O_3$ , 660 K in pure samples, shifts to lower temperatures if the oxide is mixed with Pt/NaMor and treated at elevated temperatures. Even storage at room temperature for days or weeks results in a downward shift of the TPR peak. The absence of this effect immediately after mixing is inconsistent with the primitive model of hydrogen spillover. This is the first reason for considering the presumably much slower process of a migration of Pt out of the zeolite onto the iron oxide. Also, the observation that grinding of the mixtures in a mortar is crucial for the reducibility enhancement suggests a solid state interaction. Grinding provides a most intimate contact between the two solids; virtually no reducibility enhancement is observed for gently mixed systems which behave almost as pure  $Fe_2O_3$ .

The most direct indication for Pt migration onto the  $Fe_2O_3$ particles is provided by the fact that the TPR maximum at 550 K is identical for a physical mixture after calcination and for samples in which Pt was directly supported on the  $Fe_2O_3$ . The experiments in which the Pt loading on iron oxide was varied clearly show that this TPR peak position is independent of the quantity of the platinum. Only the ratio of the fraction of  $Fe_2O_3$  reduced at this low temperature and that which is reduced at the high temperature varies with the amount of Pt. All these data suggest that the rate limiting step is different for the reduction of pure  $Fe_2O_3$  and  $Fe_2O_3$  in direct physical contact with Pt particles.

True' hydrogen spillover requires that H atoms move from the H donor to the H acceptor. When adsorption of H atoms on an oxide is vastly endothermic with respect to gaseous  $H_2$ molecules, this migration is likely to take place on two parallel 'rails': protons jump from one surface  $O^{2-}$  ion to the next while the underlying TM cations change their electrochemical valency by one unit. In other words: the oxide has to be a semiconductor with migrating n or p charge carriers.  $TiO_2$  is an oxide fulfilling these conditions and has been shown to enable classical hydrogen spillover to take place. The present data in Fig. 7 show that Pt/TiO<sub>2</sub> does indeed enhance the reduction of  $Fe_2O_3$ , as expected; but the response to dilution with a tenfold excess of  $TiO_2$  creates a broad TPR peak. This reduction rate maximum is located between the two extreme cases found on  $Pt/Fe_2O_3$ . Since in this case hydrogen has to travel over a considerable distance over the TiO<sub>2</sub> surface and cross grain boundaries until it reaches a Fe<sub>2</sub>O<sub>3</sub> particle, this process needs a higher activation energy and a wider energy distribution leading to the observed behavior. The phenomenological evidence is quite different from that shown in Fig. 5, where two discrete peaks exist which discriminate between the Pt enhanced and the not enhanced reduction of  $Fe_2O_3$ . Since  $Fe_3O_4$ , like  $TiO_2$ , is also a semiconductor, it should

also be capable of true hydrogen spillover. Indeed, the data in Fig. 8 reveal a very similar response to dilution. We wonder whether this broad TPR signal of diluted samples located between the temperature limits of the enhanced and not enhanced reduction, might be used as an experimental criterion for 'true' hydrogen spillover, distinguishing it from the reduction enhancement caused by metal migration.

The remarkable effect on  $Fe_2O_3$  reduction that is caused by minute amounts of platinum shows that a small number of Pt atoms on an Fe<sub>2</sub>O<sub>3</sub> particle suffices to enhance the reduction of that particle. This explains why Pt amounts below the detection limit of EDX suffice to induce a significant reduction enhancement. The result also shows that TPR is much more sensitive for the migration of very small amounts of Pt than EDX and other physical techniques.

In previous work of this group on physical mixtures of Pt/NaY and sulfated zirconia, migration of Pt out of a zeolite onto an oxide was proven directly. In that work more rigorous calcination conditions were applied: the mixture was treated in pure O<sub>2</sub> at 773 K for 2 h. After that treatment the presence of Pt crystallites on the surface of sulfated zirconia could be detected unambiguously by electron microscopy with EDX and by electron diffraction.13

Since Pt migration is reasonably proven the question arises, which Pt species is actually migrating, Pt<sup>0</sup> clusters, Pt<sup>2+</sup> ions or Pt oxide clusters?

The present data show that migration is pronounced after calcination in O<sub>2</sub> but non-existent with prereduced Pt/ NaMor. These results strongly indicate that metallic Pt<sup>0</sup> clusters are not the migrating species. Accordingly, the effect of Pt on the catalytic reduction of acetic acid is absent when Pt is present as Pt<sup>0</sup> inside the zeolite. For the migration after calcination Pt ions or oxide clusters remain candidates. It is known from the literature that  $PtO_2$  is volatile at elevated temperature. The equilibrium constant<sup>24,25</sup> for the reaction:

$$Pt(s) + O_2 \rightleftharpoons PtO_2(g)$$
 (4)

gives a vapor pressure of PtO<sub>2</sub> at 673 K in 1000 mbar O<sub>2</sub> of about  $2 \times 10^{-10}$  mbar. Using as an assumption a Pt particle size of 1 nm, the amount of platinum evaporated during the calcination amounts to 5 µg or ca. 1% of the Pt loading. This estimate disregards a potentially higher vapor pressure of small particles. Since the activation energy for surface migration is certainly lower than the desorption energy, it is likely that PtO<sub>2</sub> easily diffuses out of the zeolite. Therefore, it is reasonable to assume that during calcination in O<sub>2</sub> the main migrating species is PtO2, either via surface diffusion or over the gas phase. The volatility of metal oxides is known to be increased by water vapor,<sup>26</sup> which could be produced by desorption of H<sub>2</sub>O from the zeolite during calcination. Migration of PtO<sub>2</sub> also provides a plausible rationalization of results by Roessner et al.27 who observed bifunctional catalysis of *n*-hexane conversion over the acid form of erionite that had been in physical contact with Pt/Al<sub>2</sub>O<sub>3</sub> during calcination in oxygen at 723 K.

Transport of Pt as PtO<sub>2</sub> seems less plausible to explain the present finding that Pt precursors migrate even at room temperature, when given sufficient time. If Pt is reduced prior to mixing, even after six weeks storage no effect is visible on the reducibility of  $Fe_2O_3$ . Thus  $Pt^0$  clusters are obviously not able to migrate at room temperature, even over a very long time. The TPR profile D in Fig. 4 shows that after several weeks at room temperature a substantial part of the  $Fe_2O_3$  is reducible at the same low temperature as the oxide which was calcined at 673 K (profile B). As it is difficult to imagine that the extremely low vapor pressure of PtO<sub>2</sub> at room temperature can induce this Pt doping of part of the  $Fe_2O_3$ , it appears more likely that migration of Pt-ions is responsible for this low temperature transport of Pt from the zeolite to part of the  $Fe_2O_3$ . Under the TPR conditions these ions will,

of course be reduced to  $Pt^0$  clusters capable of dissociating  $H_2$ molecules. From previous work with Pt and Pd ions in zeo-lites it is known<sup>28,29</sup> that their mobility is vastly enhanced by ligands in complexes such as  $Pt(NH_3)_4^{2+}$  or  $Pd(NH_3)_4^{2+}$ . We therefore assume tentatively that the migrating individuals at room temperature during extensive storage times are hydrated ions, e.g.  $Pt(H_2O)_4^{2+}$ .

Migration of ions out of the zeolite has, however, to be compensated by a migration of other charge carriers in the opposite direction. Possible candidates for that are H<sup>+</sup> or  $Fe(OH)_2^+$  according to the following equation:

$$Fe_2O_3 + Pt^{2+} + 2 H_2O \rightleftharpoons 2 Fe(OH)_2^+ + PtO$$
 (5)

Since up to now there is no evidence for Fe in the zeolite, this mechanism remains speculative. It should be noted that a zeolite containing Fe ions might behave as a semiconductor. Indeed, the reduction profile of the mixture after storage at room temperature, has some resemblance to those which were obtained with mixtures with known hydrogen spillover.

Rather than expanding in vague speculations, we conclude that there is evidence for Pt migration in the systems studied here in agreement with our earlier results.<sup>13</sup> Mere migration of adsorbed H atoms over zeolite walls is ruled out as a major cause of the strong enhancement of the Fe<sub>2</sub>O<sub>3</sub> reduction. Migrating platinum, not spiltover hydrogen, is responsible for the non-additive catalytic signature of mixtures of Fe<sub>2</sub>O<sub>3</sub> with either Pt/SiO<sub>2</sub> or Pt/NaMor.

### Conclusions

TPR discriminates between Pt migration and 'true' hydrogen spillover. The latter phenomenon is negligible for electrically insulating oxides. In mixtures with semiconducting oxides such as TiO<sub>2</sub>, hydrogen spillover leads to broad TPR peaks located between those characteristic of unpromoted and Ptpromoted reduction of Fe<sub>2</sub>O<sub>3</sub>. In contrast, deposition of very small amounts of Pt onto Fe<sub>2</sub>O<sub>3</sub> results in TPR profiles with two discrete peaks, typical for unpromoted and Pt-promoted reduction. The intensity ratio of these TPR peaks correlates with the Pt content. Migration of Pt from mordenite cavities onto Fe<sub>2</sub>O<sub>3</sub> requires close contact, obtained by grinding the powder mixture, and oxidation. Migration of Pt<sup>0</sup> is negligible. PtO<sub>2</sub> migration via the vapor phase is conceivable, but via the surface more probable. At room temperature and in moist air, migration of hydrated Pt<sup>2+</sup> ions is the most likely cause for the enhancement of Fe<sub>2</sub>O<sub>3</sub> reduction observed after storage of the uncalcined powder mixture for weeks.

The effect of Pt in mordenite on the catalytic reduction of acetic acid over Fe<sub>3</sub>O<sub>4</sub> is entirely due to Pt migration onto the oxide. A true H spillover effect is negligible as follows from the absence of this effect in mixtures where Pt was pre-reduced and hence unable to migrate.

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