Enhanced Reduction of Fe_2O_3 Caused by Migration of TM Ions out of Zeolite Channels

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Theoretical models do not predict significant hydrogen spillover from metal particles to the surface of a nonconducting oxide in the absence of a high concentration of OH groups. This is confirmed by measuring the reduction enhancement of hematite powder that is intimately mixed with H-zeolite-supported Pt, Pd, Rh, or Co. For Pt, Pd, or Rh in various zeolites, marked shifts of the H_2 TPR peak to lower temperature are found compared to the same peak for pure Fe_2O_3. Such reduction enhancement is, however, only observed with precalcined mixtures, never with mixtures that were only reduced after grinding. This eliminates H spillover along zeolite walls as an effective mechanism. Instead, transition metals (TMs) in zeolite cavities form oxide particles which react with the protons to form TM ions during calcination. These ions migrate out of the zeolite to the iron oxide, where they can be reduced to TM metals, now positioned directly on the Fe_2O_3. This thermodynamically permitted type of H spillover to the oxide thus requires direct contact between the metal and the reducible oxide. The mechanism has general validity; however, marked differences between metals and different zeolites illustrate which factors are crucial for TM ion mobility through zeolite channels and over hematite particles. While migration of TM oxide clusters through zeolite channels is faster than migration of TM ions, ligated ions move faster than naked ions, and their migration can be accelerated by exposure to water vapor. © 2000 Academic Press

Key Words: permitted and forbidden hydrogen spillover; ion migration out of zeolites; enhanced reduction of iron oxide; diffusion across solid-phase boundaries.

1. INTRODUCTION

Many catalytic and solid-state chemical processes involve migration of atoms along the surface or in the bulk. A case in point is the reduction of hematite, Fe_2O_3, to magnetite, Fe_3O_4. For powders which were ground to introduce lattice defects, this process involves removal of oxygen from the surface and migration of Fe^{2+} ions to octahedral and tetrahedral positions in the interior (1, 2). If hydrogen is

used as the reductant, H_2 molecules must first dissociate at the surface; this step is greatly enhanced by the presence of Fe^0 or other transition metals (TMs). It is generally assumed that H atoms migrate from the TM particles to the reducible oxide; the term "hydrogen spillover" was introduced by Boudart in 1969 (3). Numerous observations have been attributed to this phenomenon (4, 5). A significant enhancement of the reduction rate is achieved by depositing Pt particles on the surface of Fe_2O_3; temperature-programmed reduction (TPR) data show that this lowers the temperature at which Fe_2O_3 is reduced by more than $100°C$ (6). This spillover process can be described as the transformation of an H atom, chemisorbed on the Pt surface, into a proton and an electron, with the proton bonded to an O^{2-} ion of the oxide and the electron reducing an Fe^{3+} ion to an Fe^{2+} ion:

$$H_{ads} \rightarrow H^+ + e^-.$$
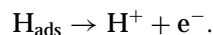
As a reducible oxide is also a semiconductor, further migration of the H atom over the surface of the oxide is then interpreted as migration of a proton–electron pair. As this model requires a finite rate of electron migration, it does not predict any mobility of spilt-over H atoms on the surface of an electrically isolating oxide, such as SiO_2, Al_2O_3, or a zeolite, except at very high temperatures.

Claims have, however, been made in the literature that hydrogen spillover including migration over large distances takes place at low temperatures over the surfaces of SiO_2, Al_2O_3, or glass; see for instance Refs. (7, 8). No identification of the state of the migrating species has, however, been presented. As electron migration appears unlikely, one could imagine that an H atom, adsorbed on the surface of a TM, might react with the proton end of an adjacent hydroxyl group of the oxide, forming an $(H_2)^+$ ion attached to the same O^{2-} ion. For the reaction of a free proton with an H atom spectroscopic data predict an exothermicity of $2.6507 \text{ eV} = 255.7 \text{ kJ mol}^{-1}$ (9). When considering that the energy of an H atom on a TM surface is roughly 255 kJ/mol lower than that of a free H atom, such a process appears thermodynamically plausible. For the H migration over the oxide surface, it requires, however, a high density of

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hydroxyl groups so that a process of the type

$$(H_2)^+–O^{2-} + H^+–O^{2-} \rightarrow H^+–O^{2-} + (H_2)^+–O^{2-}$$
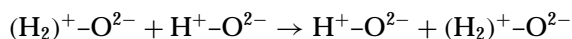
would permit the spilt over H atoms to spread over the surface to regions far from the metal/oxide interface.

An alternative model, assuming that the migrating individuals are physisorbed H atoms on the oxide surface, can be excluded on thermodynamic grounds. Using conventional values of the energy of physisorption by van der Waals–London interaction and the measured heats of adsorption of hydrogen on transition metals, the spillover step would be endothermic by more than 230 kJ/mol of H, which is incompatible with the claimed migration rates at moderate temperatures.

This leaves open the question of whether any H spillover is possible on nonconducting, unreducible oxides in the absence of a high density of surface OH groups. For instance, for H atoms adsorbed on Pt particles inside the cavity of a dehydrated zeolite none of the above models predicts H spillover onto the zeolite walls or H migration out of the zeolite to some suitable acceptor, such as a reducible oxide.

Previous TPR work in this laboratory showed that in physical mixtures of Fe₂O₃ with a zeolite containing Pt particles in its cavities, the reduction of the Fe₂O₃ was dramatically enhanced. It was shown that this effect was *not* caused by hydrogen migrating along zeolite walls, but rather by migration of Pt oxide clusters. These crawl out of the zeolite onto the iron oxide, where they will be converted to Pt⁰ clusters under reducing conditions (6, 10). As Pt oxides have a much higher surface mobility than Pt⁰ clusters, no reducibility enhancement was observed in mixtures of iron oxide with *prereduced* Pt-containing zeolites, whereas the TPR peak for Fe₂O₃ reduction to Fe₃O₄ was found to be markedly shifted to lower temperature for mixtures that had been calcined in O₂ at 500°C. As platinum, palladium, and rhodium oxides have different mobilities, marked differences were found in their effects on the reducibility of Fe₂O₃ (11).

In nonacidic zeolites such as NaMor, TM oxides are easily formed by first reducing the ion-exchanged system with H₂, and then calcining the *Me*⁰/zeolite in O₂. It is well known that in acidic zeolites, such as the H form of mordenite, the same treatment will entail protonolysis; i.e., the TM oxide clusters will be converted into TM ions + H₂O which is desorbed (12). It is, therefore, possible to study the mobility of TM ions out of the zeolite onto an admixed iron oxide, by starting from the H form of the zeolites and further following the procedure described above. Preliminary results have been reported in Ref. (10). The main objective of the present research is to compare the migration of TM ions with that of oxide clusters of the same TM and to register their effect on the reduction of Fe₂O₃ in ground physical mixtures.

There are, however, a number of complicating phenomena which have to be considered in applying this strategy:

Upon heating H-zeolites containing TM ions, dealumination and loss of crystallinity of the zeolite can occur (13).

To maintain electroneutrality, TM cations or protons moving out of a zeolite will be replaced by other cations moving in (14). In the mixtures of interest in this work, part of the Fe₂O₃ may thus be destroyed and Fe³⁺ ions are expected to migrate into zeolite cavities.

Under calcination conditions the TM ions leaving the zeolite will interact with the Fe₂O₃. Solid solutions such as Co$_x$Fe$_{2-x}$O₃ or Co$_x$Fe$_{3-x}$O₄ or spinels such as CoFe₂O₄ might be formed. As these processes will lower the Gibbs free energy of the oxides, they could result in lower reducibility. Moreover, if these interactions lead to strong anchoring of the TM ions on the surface of the first Fe₂O₃ particle which they encounter, they might leave the reducibility of more remote particles unaffected. Obviously, this should be apparent when comparing mixtures with different ratios of Fe₂O₃ and the zeolite in the mixture.

2. EXPERIMENTAL

The following zeolites were used: Na-mordenite (NaMor) with Si : Al = 6.5 (Zeolyst International, lot 1822-50), NaZSM-5 with Si : Al = 13.5 (ALSI-PENTA Zeolithe SN 27), and NH₄-BEA with Si : Al = 12.5 (Zeolyst International, lot 814E-208-D). The NH₄ forms of mordenite and ZSM-5 were obtained from the Na forms by ion exchange with NH₄NO₃. Metal-containing zeolites were obtained by ion exchange of the ammonium forms. The following salts were used for the exchange: Pt(NH₃)₄(NO₃)₂, Pd(NH₃)₄(NO₃)₂, Rh(NH₃)₅Cl₃, and Co(NO₃)₂ · 6H₂O. The metal loading was 5.1×10^{-5} mol/g in all cases. The zeolites were slurried in water (200 ml/g). Diluted salt solutions were added dropwise at room temperature to the stirred slurries except for the Rh salt, which was added at 363 K. Stirring was continued for 72 h, and then the samples were filtered, washed, dried in air, calcined in an O₂ flow (300 ml/min) with a heating rate of 0.5 K/min up to 773 K, and then kept at 773 K for 4 h. Finally, the samples were reduced in 5% H₂/Ar (Pt-, Pd-, and Rh-containing samples) or in pure H₂ (Co-containing sample). The temperature was increased to 773 K with a ramp of 8 K/min and held at 773 K for 0.5 h.

Physical mixtures of reduced *Me*/zeolites with Fe₂O₃ were prepared by grinding in a mortar inside a nitrogen-filled glove box. The content of Fe₂O₃ in the mixtures varied from 2.4 to 84 wt%.

As-prepared (further called "reduced") or calcined mixtures were studied. The standard calcination was performed with a ramp of 8 K/min to 773 K and held at 773 K for 10 min. Where different calcination conditions were used, the details are described in the text. In some cases, water vapor

pretreatment was used; it was carried out in an oxygen flow passing through a water saturator in an ice trap.

The mixtures were characterized by temperature-programmed reduction (TPR). TPR was carried out with 100-mg samples in a flow of 5% H_2/Ar with a rate of 30 ml/ min and a heating ramp of 8 K/min. Only the first reduction stage—reduction of Fe_2O_3 to Fe_3O_4—was studied in detail. The hydrogen consumption was monitored by TCD.

Powder XRD patterns were detected in air on a Rigaku diffractometer with Co $K\alpha$.

3. RESULTS

*Metal Reduction and Chemical Interaction
with Zeolite Matrix*

When TPR profiles are registered, the metals platinum, palladium, and rhodium in the calcined mixtures are always reduced first at rather low temperatures, before the reduction of hematite is observed. The metal reduction peaks are hardly visible in most of the following figures, but can easily be seen by appropriate amplification of the TPR profiles. However, with Co/zeolites no peaks are observed at low temperatures.

XRD was used to probe selected samples (reduced Pd/HZSM-5, and hematite mixtures with Pd/HZSM-5 and Pt/HZSM-5) for changes in crystallinity. No signs of decrease of zeolite crystallinity or formation of new compounds were observed.

*Reduction of 1 : 1 Fe_2O_3 Mixtures with Me/HZSM-5,
Me/HMor, and Me/HBEA*

The TPR profiles of all mixtures with equal mass amounts of Fe_2O_3 and reduced *Me*/HZSM-5 (*Me* = Pt, Co, Pd and Rh) consist of a single peak (Fig. 1). For *Me* = Co, the peak position coincides with that of pure hematite as it was always observed with reduced samples. It was unexpected, however, that the profiles of Rh- and Pd-containing mixtures had their maxima shifted to higher temperatures than with pure hematite. The temperature shift is 30 K for Rh and 40 K for Pd. A very small shift for Pt follows the same trend, but is within experimental error. Shifts to higher temperature were never observed in previous studies. The TPR profile of a mixture of Fe_2O_3 with metal-free HZSM-5 is also included in Fig. 1. The maximum of this profile is located at 670 K, so the upward shift of the metal-containing samples cannot be attributed to the presence of an H-zeolite.

For comparison with the prereduced samples the TPR profiles of calcined mixtures are presented in Fig. 2. The signature of Pt in HZSM-5 is quite similar to that of Pt in Na-zeolites (6, 11). The reduction enhancement caused by migration of Pt ions is quite obvious: the Fe_2O_3 reduction peak is shifted downward to 550 K. Cobalt does not affect the reducibility of hematite; Rh exhibits some enhanced reduction, but the pattern is rather complicated. Most surprising
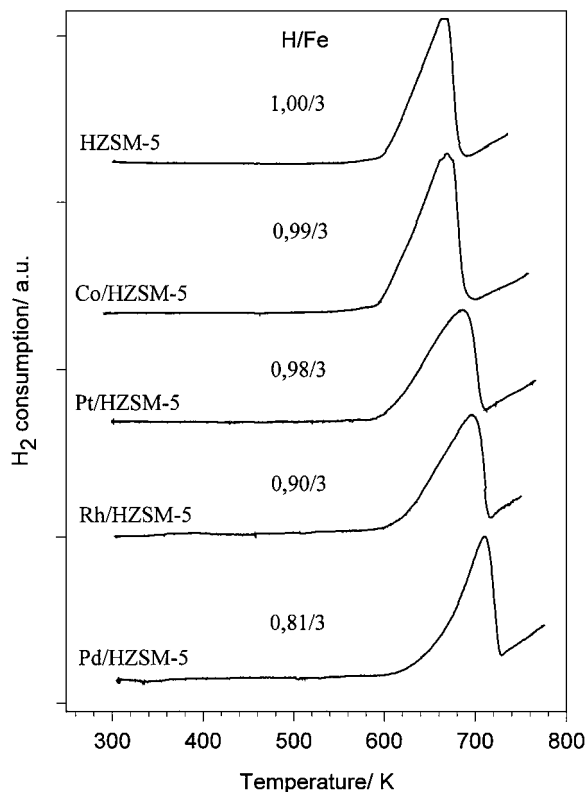

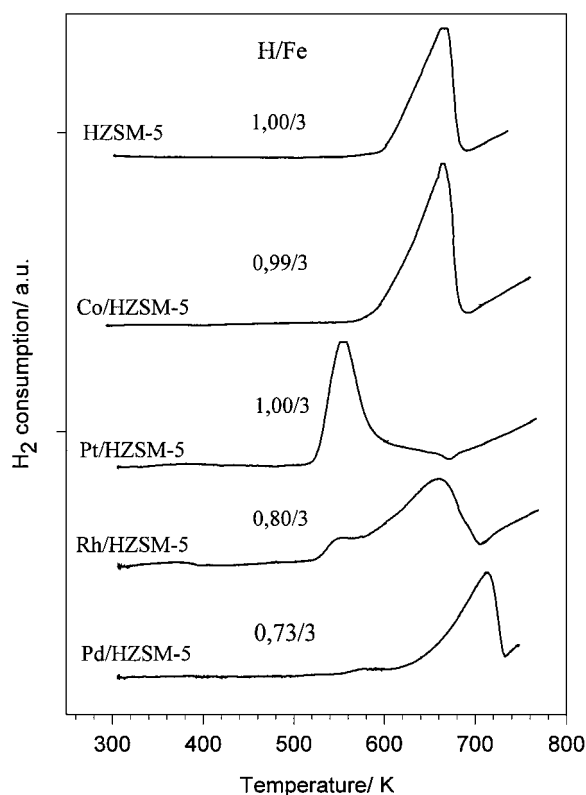**FIG. 1.** TPR profiles of 1 : 1 Fe_2O_3 mixtures with reduced *Me*/HZSM-5.

FIG. 2. TPR profiles of calcined 1 : 1 Fe_2O_3 mixtures with *Me*/HZSM-5.
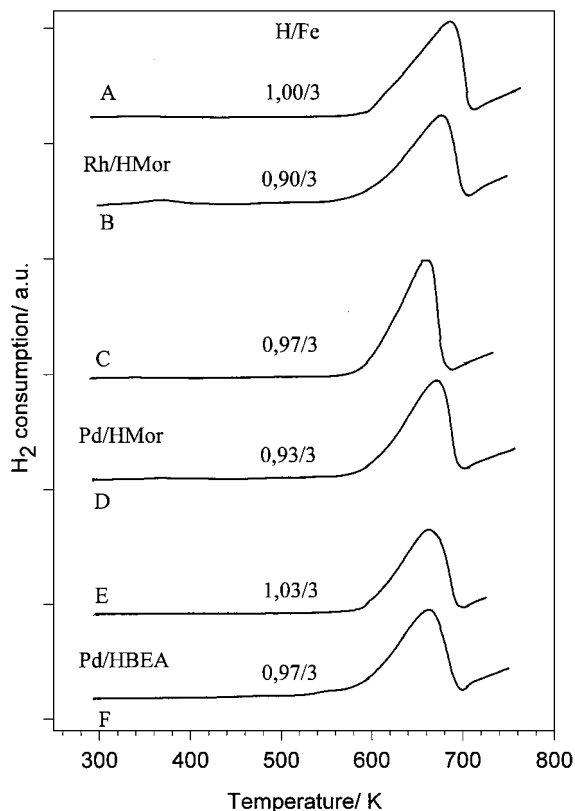
FIG. 3. TPR profiles of 1 : 1 Fe₂O₃ mixtures with Rh/HMor, Pd/HMor, and Pd/HBEA: (A, C, E) the mixtures with reduced *Me*/H-zeolites; (B, D, F) calcined mixtures.

corresponds to the calculated value of 1/3 within experimental error. No effects on hematite reduction are detected in the TPR profiles of calcined mixtures (Fig. 3, curves B, D, and F). No change in peak position or H/Fe ratio is observed.

Effect of Pretreatment on the Reducibility of Fe₂O₃ Mixtures with Me/H-Zeolites

As the results described above could indicate that migration of rhodium and palladium ions out of the zeolites is slower than that of platinum, long-term calcination of Rh- and Pd-containing mixtures was performed (2 h instead of the standard 10 min). The results showed that the TPR profiles of Fe₂O₃ mixtures with Rh/HMor (Fig. 4, curve C), Pd/HMor (Fig. 5, curve C), and Pd/HBEA (Fig. 5, curve E) were not affected by this extended calcination. However, the profiles of the mixtures Fe₂O₃ + Rh/HZSM-5 (Fig. 4, curve A) and Fe₂O₃ + Pd/HZSM-5 (Fig. 5, curve A) showed a change in shape. A small peak of promoted reduction appeared in the profile of the Pd-containing mixture; it corresponded to approximately 15% of total hematite reduction. The resulting profile of the Rh-containing mixture became broad, resembling the profiles of Rh/Fe₂O₃ and Fe₂O₃ mixtures with Rh/Na-zeolites (11).

is Pd/HZSM-5; it not only shows no enhanced reduction, but actually shifts the TPR peak of Fe₂O₃ to higher temperature, a phenomenon reminiscent of the mixture with prereduced Pd.

In Figs. 1 and 2 also the hydrogen consumption is shown, calculated from integration of the peak area. Ideally, an H/Fe value of 1/3 is expected for

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O.$$
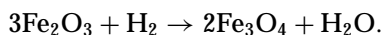
The observed values for mixtures with Pt- and Co-containing zeolites are equal to this number within experimental error. However, for Pd- and Rh-containing mixtures the observed values are lower, in particular for the calcined samples; it follows that the absence of a downward shift of the TPR peak is paralleled by incomplete reduction of hematite to magnetite.

The absence of a marked downward peak shift in mixtures with Pd is not typical for the HZSM-5 support; qualitatively similar results are found with HMor and HBEA, as shown in Fig. 3. With the reduced samples, Pd/HMor and Pd/HBEA as well as Rh/HMor (Fig. 3, curves C, E, and A), the reduction peaks are located near 670 K, i.e., the peak position of pure hematite. The H₂ consumption
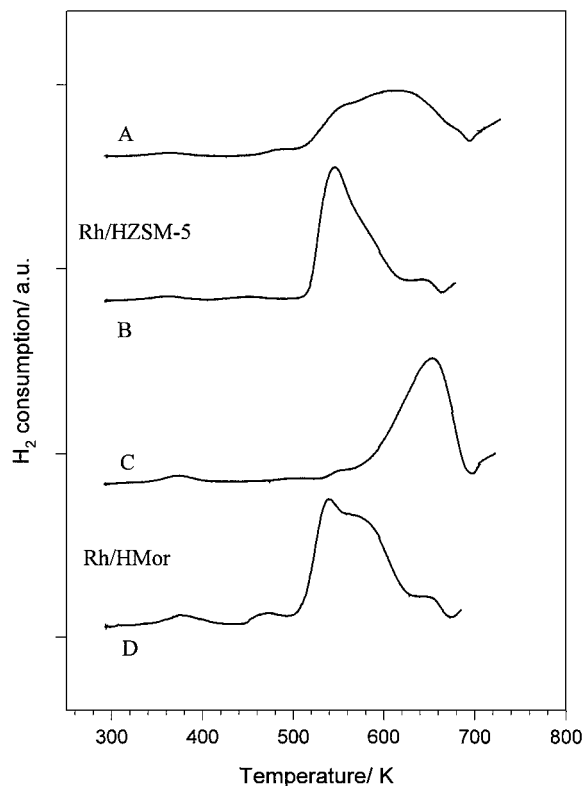

FIG. 4. Effect of exposure to H₂O vapor on the TPR profiles of 1 : 1 Fe₂O₃ mixtures with Rh/H-zeolites: (A, C) after calcination for 2 h; (B, D) after heating in H₂O/O₂ and subsequent calcination.
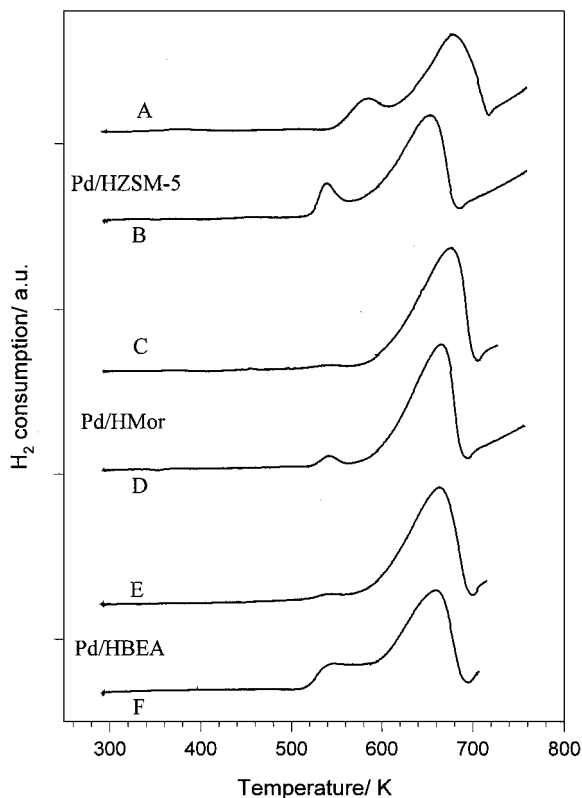
FIG. 5. Effect of exposure to H_2O vapor on the TPR profiles of $1:1$ Fe_2O_3 mixtures with Pd/H-zeolites: (A, C, E) after calcination for 2 h; (B, D, F) after heating in H_2O/O_2 and subsequent calcination.

Our previous study (10) demonstrated that exposure to water vapor facilitates the migration of platinum ions in HMor. In the present work this effect was studied with Rh- and Pd-containing mixtures. They were heated in a water/oxygen flow to 770 K with a ramp of 8 K/min and held for 1 h. This was followed by calcination in dry oxygen at 770 K for 1 h, so the total treatment time was equal to that in the long-term calcination. The data in Figs. 4 and 5 clearly demonstrate the positive effect of exposure to water vapor: it causes a dramatic change of the TPR profiles of Rh-containing mixtures (Fig. 4, curves B and D); also in the mixtures with Pd/HMor and Pd/HBEA an enhanced reduction of part of the hematite is visible (Fig. 5, curves D and F). The influence of water vapor on the peak area ratio and the H/Fe ratio in the profile of Pd/HZSM-$5 + Fe_2O_3$ is negligible, but the peak position is clearly affected (Fig. 5, curve B). After the exposure to water vapor, a downward shift of both parent peak and satellite is obvious.

There appears to be a general trend that the effect of the metal on the reduction of hematite depends on the zeolite support; the effects of the pretreatments are less pronounced with HMor-based samples than with those supported in HZSM-5 or HBEA.

Effect of Mixture Composition on TPR Profiles of Calcined Fe_2O_3 Mixtures with Me/H-Zeolites

Before grinding, the Fe_2O_3 particles are larger than the zeolite particles. For the mixing ratios used here, every Fe_2O_3 particle will be in contact with a zeolite; migrating transition metal species have to pass one phase boundary to decorate all Fe_2O_3 particles. The situation after grinding is less clear, because particles will be crushed. To get some impression of how reducibility enhancement depends on the required migration path and the need of transition metal species to move between Fe_2O_3 particles, experiments were done with different Me/zeolite-to-Fe_2O_3 ratios.

With Co/HZSM-$5 + Fe_2O_3$ it was found that increasing this ratio by a factor of 10 did not affect the peak position in the TPR profile. Obviously, the absence of any reducibility enhancement for this system is not caused by insufficient intergranular contact of Co-zeolite and Fe_2O_3 particles.

For Pt-containing mixtures the results are shown in Fig. 6. While reduction always occurs at a lower temperature than in the absence of Pt, the TPR peak positions of the mixtures with low hematite content appear at somewhat higher temperatures than found for the mixtures with Pt/NaZSM-5. Reduction maxima of Fe_2O_3 mixtures with Pt/HZSM-5 are located at ca. 550 K (Fig. 6), while the peaks for
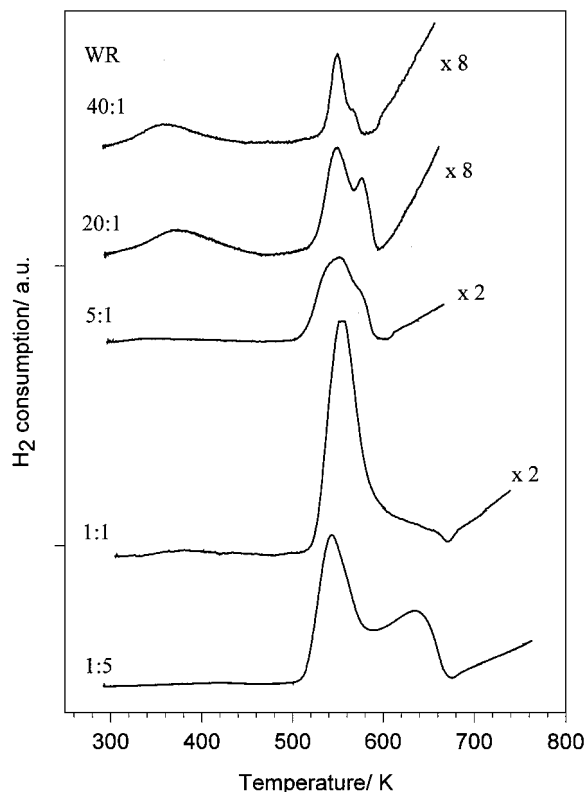

FIG. 6. Effect of zeolite/hematite mass ratio on TPR profiles of calcined Fe_2O_3 mixtures with Pt/HZSM-5. Mass ratio Pt/HZSM-5 : Fe_2O_3 (MR) is indicated in the figure.

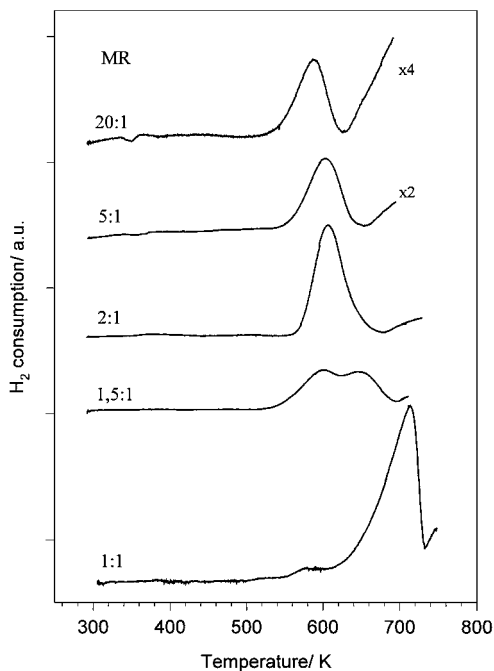**FIG. 7.** Effect of mixing ratio on TPR profiles of calcined Fe₂O₃ mixtures with Pd/HZSM-5. Mass ratio Pd/HZSM-5 : Fe₂O₃ (MR) is indicated in the figure.

FIG. 8. Effect of mixing ratio on TPR profiles of calcined Fe₂O₃ mixtures with Rh/HZSM-5. Mass ratio Rh/HZSM-5 : Fe₂O₃ (MR) is indicated in the figure.

$Fe_2O_3 + Pt/NaZSM\text{-}5$ were at 500–510 K (11). Moreover, some peaks are now split, resembling the profiles of Fe_2O_3 mixtures with Pd/NaZSM-5 (11) though splitting is more pronounced with Pt.

Figures 7 and 8 show TPR profiles of mixtures with Pd/HZSM-5 and Rh/HZSM-5 with a different weight ratio of Me/HZSM-5 to Fe_2O_3. The TPR profiles in the figures show that the zeolites can provide a completely enhanced reduction of certain amounts of Fe_2O_3 even after the brief standard calcination. A comparison of the results with the data obtained for Me/NaZSM-5 (11) shows the same tendency as in the case of Pt: the mixtures with low hematite content are reduced at lower temperatures if the zeolite is used in the Na form, whereas the reduction temperatures for the samples prepared with HZSM-5 are higher. For instance, the TPR profile of the 20 : 1 Pd/HZSM- 5 mixture has its maximum at 585 K, while Pd/NaZSM-5 causes a lowering of the reduction temperature to 530 K. The comparison for Rh-containing samples gives the values 555 and 525 K, respectively.

To study the effect of the zeolite in which the metal is entrapped, Pd is compared with HMor, HBEA, or HZSM-5 as the support. The Pd/HMor mixture with hematite with a weight ratio of 5 : 1 gives rise to a TPR profile in which the peak of unpromoted reduction dominates (see Fig. 9). In contrast, mixtures of Pd/HZSM-5 and Fe_2O_3 with the same or an even higher hematite content are still reduced at lower temperatures (see Fig. 7). The profile of Pd/HBEA in Fig. 10 is similar to that of Pd/HZSM-5 in Fig. 7.
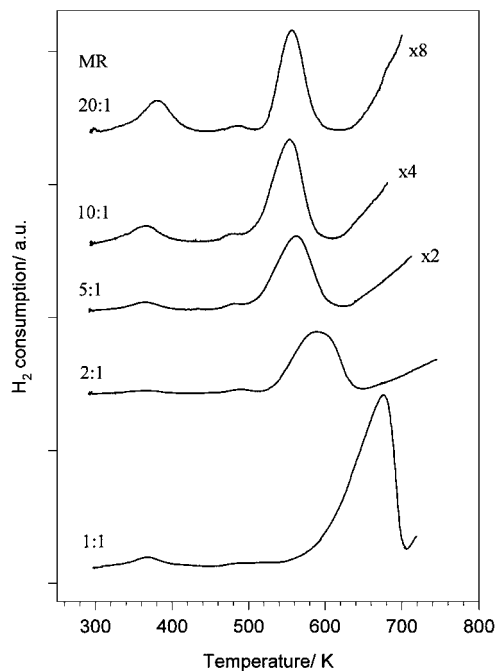

FIG. 9. Effect of mixing ratio on TPR profiles of calcined Fe₂O₃ mixtures with Pd/HMor. Mass ratio Pd/HMor : Fe₂O₃ (MR) is indicated in the figure.

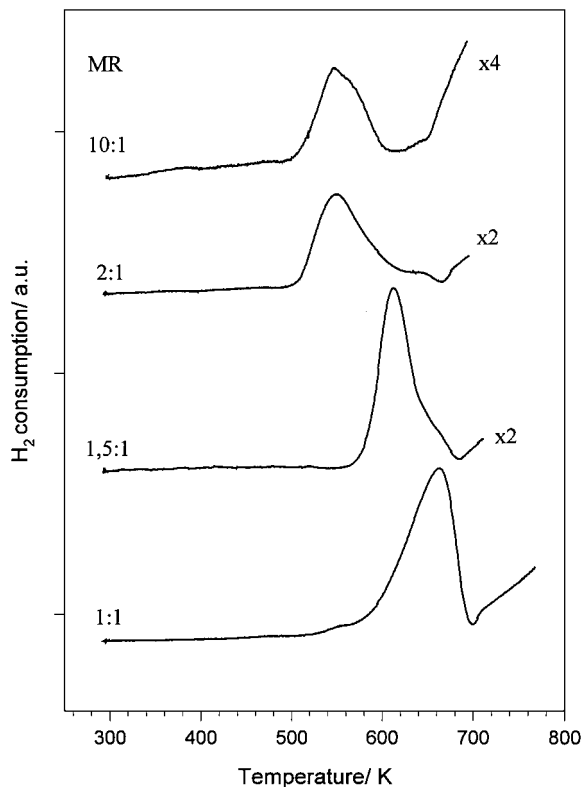**FIG. 10.** Effect of mixing ratio on TPR profiles of calcined Fe_2O_3 mixtures with Pd/HBEA. Mass ratio Pd/HBEA : Fe_2O_3 (MR) is indicated in the figure.

4. DISCUSSION

The general model for enhanced reducibility emerging from the present results is that cations of platinum, palladium, or rhodium are formed inside zeolite channels by protonolysis of TM oxide clusters. The TM cations are able, under certain conditions, to migrate from zeolites onto the iron oxide surface. In a reducing atmosphere they will be reduced to TM clusters, decorating the Fe_2O_3 surface, and H_2 will be dissociatively chemisorbed on them. True H spillover from the TM to the oxide surface initiates the reduction of the latter at a lower temperature than in the absence of the TM mediator. Of the TM/zeolite systems studied, the Co-containing zeolites do not enhance the reduction of Fe_2O_3, because Co ions are not reduced to Co metal clusters.

The present TPR data provide two criteria for assessing the effect of the TM/zeolites on the reducibility of Fe_2O_3: (a) the position of the TPR peak(s) with respect to that of pure Fe_2O_3, and (b) the extent of the reduction obtained by the integration of the TPR peak. Both criteria show that migration of TM cations (in H-zeolites) is significant, but less efficient than the migration of oxide clusters of the same transition metal (in the Na-zeolites) in enhancing the reducibility of Fe_2O_3. However, TM cation migration through

zeolite channels can be accelerated by adding appropriate ligands to them. This was shown previously for the addition of NH_3 ligands to TM cations in zeolite channels (15–17). In the present work, exposure of the mixtures to water vapor was found to enhance the reduction of the Fe_2O_3. Apparently, the TM cations are transformed to their aquo complexes which are less strongly held at the walls of the zeolite cavities. As a result of the enhanced cation mobility, a higher extent of reduction enhancement is achieved, as shown in the present work and in previous research on mixtures of hematite with Pt/HMor (10).

From an analysis of the peak positions it follows that the mobility of the TM ions through the channels depends on the type of the zeolite. For rhodium Fig. 3 shows that in HMor this TM does not cause any peak shift (in the absence of water), but in HZSM-5 it exerts a strong effect on the reducibility of the hematite, as is obvious from Fig. 2. Likewise, for palladium Fig. 5 reveals marked differences between Pd/HZSM-5, Pd/HBEA, and Pd/HMor.

Still focusing on peak positions, it is of interest that with some mixtures the TPR peak is shifted to slightly higher temperatures in comparison to pure hematite. Figure 1 shows some examples. In the Introduction it was mentioned that some TM oxides form solid solutions or solid compounds with Fe_2O_3. Ion migration will be an efficient vehicle for these processes; it is conceivable that Fe^{3+} ions in a binary oxide with lower free energy than Fe_2O_3 will be more difficult to reduce than pure Fe_2O_3.

Turning now to the extent of reduction, which is obtained from integrating the TPR peaks, and the related phenomenon of splitting in multiple peaks, it might be helpful to first recall Gibbs's phase rule and the phase diagram of the iron/oxygen system. As FeO is thermodynamically unstable below $560°C$ (18), it follows that in equilbrium below $560°C$ any reduction beyond Fe_3O_4 should give Fe metal. Only after the Fe_2O_3 phase has disappeared can the reduction of Fe_3O_4 to Fe start. The present data show that this point, where one-third of all Fe^{3+} ions is reduced to Fe^{2+}, is marked by a minimum in the TPR profile.

Thermodynamics does not specify a mechanism. Colombo et al. argued that traces of Fe^0 might be present while Fe_2O_3 is being reduced to Fe_3O_4 and this Fe^0 might be instrumental in dissociating H_2 molecules (1). If this is correct, it can be assumed that migrating transition metals such as Rh or Pd would form bimetal clusters. Such a process would blur the clear minimum postulated by thermodynamics to neatly separate reduction to Fe_3O_4 from reduction to Fe^0 and thus also affect the peak integration values.

It follows from the charge conservation principle that when TM ions and protons move out of the zeolite, their charge must be compensated. If this is achieved by Fe ions migrating into the zeolite, they will be reduced to Fe^{2+} or even form an alloy with the TM particles inside the zeolite cavities, as was found previously (19, 20). This could cause

an H_2 consumption exceeding that expected for mere reduction of Fe_2O_3 to Fe_3O_4. Such additional reduction processes inside the zeolite will be accompanied by formation of protons, for instance:

$$Fe^{3+} + Rh^{3+} + 3H_2 \rightarrow (FeRh)^0 + 6H^+.$$
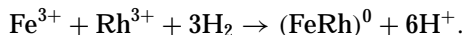
The formation of $PdFe_x$ and $RhFe_x$ clusters inside zeolite channels was proven by a special TPR/TPD technique and by Mössbauer spectroscopy (19, 20). In the present work, however, the ratio of all reducible ions inside the zeolite to the Fe ions in the iron oxide phase is so small that the expected excess of H_2 consumption over and above that required to reduce hematite to magnetite is below the experimental error of measuring H_2 consumption.

Multiple and "blurred" TPR peaks are typically observed, where migrating TM ions succeed at initiating the reduction process at rather low temperatures. In contrast, nice regular peaks are observed where reduction is *not* enhanced (see the curves in Figs. 1 and 2). It is clear that the creation of a new iron oxide phase entails considerable reorganization of the iron ions and, to a lower extent, of those oxide ions which are not removed. If this process takes place at lower temperatures, the speed of the ion displacements will critically depend on the proximity of lattice defects. We can imagine that in powders such as those studied here, different regions in the bulk of each grain then display different reactivities at low temperatures.

This is discerned from peak splitting, caused by a different phenomenon. In a physical mixture of two powders some hematite particles will be in intimate contact with a TM-loaded zeolite, others will not. In such a situation, the slow migration of TM ions over a variety of phase boundaries could affect the extent of reduction derived from TPR peak integration. For illustration it may be useful to consider the extreme case in which the TM ions migrate out of their original positions inside the zeolite channels to an adjacent Fe_2O_3 particle, but become so firmly anchored on that particle that further migration over another grain boundary will be impeded. In this case, only those Fe_2O_3 particles will be reduced to Fe_3O_4 at low temperatures which are in direct physical contact with a zeolite acting as a donor of TM ions. Other Fe_2O_3 particles located farther away would only be reduced at higher temperatures and a two-peak TPR pattern will arise. These considerations motivated the experiments with widely different zeolite-to-hematite ratios, described in the present paper. This strategy assumes that with a large zeolite-to-hematite ratio almost all hematite particles are embedded in an environment of potentially TM-donating zeolite particles, but if the ratio is low, one expects part of the hematite reduction to depend on migrations of the TM precursor over several phase boundaries.

When focusing on this aspect, the present results indicate that platinum ions become rather evenly distributed over the hematite particles. Figure 6 shows that varying the mass ratio of Pt/HZSM-5 to hematite over a factor of 200 from 1 : 5 to 40 : 1 leaves the main peak near 550 K, but satellites at higher temperatures are visible even for these mixtures. The effect of the mass ratio on the TPR peak positions is stronger for the mixtures of hematite with Pd/HZSM-5 or Rh/HZSM-5, as is evident from Figs. 7 and 8.

The totality of these results, therefore, indicates that migration of TM ions

(1) through the zeolite channels,
(2) over the phase boundary between zeolite and hematite, and
(3) between hematite particles

all contribute to the observed TPR patterns. As intuitively expected, the hematite particles in most intimate contact with the TM-loaded zeolite particles will have the greatest chance to become covered with some easily reducible TM ions, possibly even forming binary oxides at the surface. Once these TM ions are reduced to TM clusters, direct hydrogen spillover can start and those hematite particles that are decorated with TM clusters will be reduced easily. The hematite particles which do not carry any reduced TM clusters at their surface then depend on a less easy type of H spillover, still using migration of protons and electrons, but including some crossing of phase boundaries.

5. CONCLUSIONS

Ions of platinum, palladium, and rhodium are able to migrate from H-zeolites onto the surface of admixed iron oxide. Once they are reduced there, the metals cause an enhancement of Fe_2O_3 reduction. The extent of the reduction enhancement depends on the metal as well as on the type of zeolite. Platinum is most efficient, presumably due to the high mobility of the ions; with Pt/H-zeolites enhanced reduction is complete with 1 : 1 mixtures. This is never observed for 1 : 1 mixtures of Rh/H-zeolites or Pd/H-zeolites with the same metal loading. Exposure to water vapor accelerates the ion migration of both rhodium and palladium through the zeolites and also the reduction of the hematite, but enhanced reduction remains incomplete, except for mixtures with very large mass excess of the Rh/H-zeolite over the hematite. Migration of palladium and rhodium out of HMor seems to be more difficult than that out of HZSM-5 and HBEA. Chemical anchoring of palladium and rhodium ions on the hematite surface inhibits their migration from one hematite particle to the next.

The results confirm the previous findings that migration of reduced TM clusters across phase boundaries is much slower than migration of oxide clusters or ions. They also show that no hydrogen spillover from zeolite-encaged TM clusters to extrazeolite Fe oxide particles is detected under conditions where reducibilty enhancement due to oxide or ion migration is obvious.

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