

Metal Migration from Zeolites onto Iron Oxide: An Alternative to Hydrogen Spillover

Olga E. Lebedeva,¹ Wen-An Chiou,² and Wolfgang M. H. Sachtler³

V. N. Ipatieff Laboratory, Center for Catalysis and Surface Science, Northwestern University, Evanston, Illinois 60201

Received June 4, 1999; revised September 7, 1999; accepted September 10, 1999

The reduction of physical mixtures of Fe₂O₃ with transition metal-containing zeolites was studied. Two zeolites (Na-mordenite and Na-ZSM-5), each loaded with one of four metals (Pd, Rh, Co, Ni), were mixed with Fe₂O₃, ground, and subjected to various treatments. Temperature-programmed reduction of these mixtures was compared with that of Fe₂O₃ onto which the transition metals had been deposited by wet impregnation. The extent by which the reduction of Fe₂O₃ is enhanced in the mixtures depends on the pretreatment and the nature of the metal, while the zeolite structure has little effect. Reduced metal clusters do not show observable migration. Crucial is the migration of metal oxide clusters out of the zeolite onto Fe₂O₃. Mobility of PtO₂ is high on zeolite walls and the Fe₂O₃ surface. PdO is rather immobile in the zeolite. Rhodium oxides, Rh₂O₃ or RhO₂, migrate through zeolite channels but appear rather immobile on the surface of Fe₂O₃. The arrival of Pt and Rh on Fe₂O₃ has been detected by transmission electron microscopy and X-ray energy dispersive spectrometry. On reduction of the oxide particles on the Fe₂O₃ surface at low temperature, H spillover and significant reduction enhancement of Fe₂O₃ take place. No H spillover through zeolite channels has been detected. © 1999 Academic Press

Key Words: reduction enhancement by Pt, Pd, Rh Ni, Co; hydrogen spillover; surface migration of oxides; temperature-programmed reduction of iron oxide.

I. INTRODUCTION

The reduction with hydrogen of oxides, such as WO₃ (1), NiO (2), V₂O₅ (3), Fe₂O₃, Co₃O₄, UO₃, MnO₂ (4), and CuO (5), is significantly accelerated in contact with transition metals. Temperature-programmed reduction (TPR) then shows that the peak characterizing the reduction of the oxide is strongly shifted to lower temperature. Early pub-

lications on this phenomenon are summarized in a number of review papers (6–8). Where direct contact between transition metal and reducible oxide exists, one can assume that H₂ molecules dissociate on the metal surface and H atoms cross the interface to the oxide. The term *hydrogen spillover*, introduced by Boudart (9), adequately describes this phenomenon.

Enhanced reducibility has also been observed for systems in which a transition metal and a reducible oxide are present on a common support, such as silica, alumina, or a zeolite, and direct contact of the metal with the reducible oxide is not obvious. In such cases it has often been assumed that transport of the H atoms consists of three steps: (1) crossing of the phase boundary between metal and support, (2) migration over the support and (3) attachment to an O²⁻ ion of the reducible oxide. For the migration of H atoms over an oxidic support, the usual implication is that H⁺ ions jump from one surface O²⁻ ion to the next, while electrons migrate below the surface. The latter assumption requires, however, that the oxide is an electric semiconductor. For Al₂O₃, SiO₂ or zeolite supports this would require doping with ions that can change their valency fairly easily.

In previous papers we have shown that no H spillover, as defined above, occurs with physical mixtures of Pt/zeolites + Fe₂O₃ at moderate temperatures (10, 11). Still, the presence of the platinum can enhance the reduction of the hematite rather dramatically, if the mixture is thoroughly ground and calcined at high temperature. In that work, clear evidence was obtained that platinum migrates out of the zeolite cavities onto the iron oxide. The migrating species are neither H atoms nor Pt⁰ atoms or Pt⁰ clusters, but oxidized forms of the platinum. In the case of Pt/NaMor, Pt oxide clusters, presumably PtO₂, migrate, while in the case of an acid zeolite such as Pt/HMor, Pt²⁺ ions are the predominant migrants. Once reducing conditions are applied in a TPR run, these migrants on the surface of Fe₂O₃ become Pt clusters and true hydrogen spillover could take place. Transmission electron microscopy (TEM) and X-ray energy dispersive spectrometry (EDS) provided conclusive evidence that after the calcination treatment some Pt was positioned on the Fe₂O₃ surface.

¹ On leave from Kazakh State National University, Almaty, Republic of Kazakhstan.

² Current address: Materials Research Center, Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60201.

³ To whom correspondence should be addressed. Fax: (847) 467-1018. E-mail: wmhs@nwu.edu.

These conclusions, though conceivably of general validity, were based on data obtained with mixtures of Fe_2O_3 with Pt/Mor. The objective of the present work is to probe for the generalization by studying similar mixtures with other zeolites, in particular ZSM-5, and other transition metals, in particular Pd, Rh, Co, and Ni. The study is restricted to the Na forms of zeolites where oxidation is expected to convert metal clusters into oxide clusters. Previously we showed (11) that in the acidic form of zeolites metal ions are formed and that their mobility is affected by water.

Thus far, little is known about the effect of metals, other than platinum, on the reducibility of Fe_2O_3 . Some lowering of the reduction temperature by cobalt was reported for a coprecipitated cobalt-iron-alumina catalyst (12). For the reduction of CuO, it was reported that dopants such as Cr, Mn, Fe, Co, and Ni had no effect on the reducibility (5), whereas the presence of 2 mol% Pt, Pd, Ag, Au, Rh, Ru, or Ir resulted in significant changes in the TPR profile of CuO. They consisted of two or three peaks, most of them being shifted 100–150 K to the lower temperature in comparison to the TPR peak of pure CuO. Similar effects will be expected when these metals are in direct contact with Fe_2O_3 . However, when any of these metals is initially present in a zeolite, its effect on the reduction of admixed Fe_2O_3 will depend on the mobility of the corresponding oxide clusters and/or metal ions over the zeolite walls and the Fe_2O_3 surface. It is not obvious *a priori* how other transition metals will differ from platinum in these oxidation and transport processes and what factors are crucial for the phenomenon of enhanced reduction.

II. EXPERIMENTAL

Fe_2O_3 (hematite, J. T. Baker Chemicals; 99.5% purity) was used as supplied. Pd/ Fe_2O_3 , Rh/ Fe_2O_3 , Ni/ Fe_2O_3 , and Co/ Fe_2O_3 were prepared by incipient wet impregnation of Fe_2O_3 with aqueous solutions of the corresponding salts [Pd(NH_3)₄(NO₃)₂, Rh(NH_3)₅Cl₃, Ni(NO₃)₂·6H₂O, and Co(NO₃)₂·6H₂O]. Impregnated samples were dried in air and calcined in O₂ flow. Metal-containing zeolites were obtained by ion exchange of the sodium form. The zeolites used were Na-mordenite (NaMor) with Si:Al = 6.5 (Zeolyst International, Lot 1822-50) and NaZSM-5 with Si:Al = 13.5 (Alsi-Penta Zeolithe SN 27). The following salts were used for ion exchange: Pd(NH_3)₄(NO₃)₂, Rh(NH_3)₅Cl₃, Co(NO₃)₂·6H₂O, Ni(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, then the samples were filtered, washed, dried in air, calcined in O₂ flow (300 ml/min) with a heating rate of 0.5 K/min up to 773 K, and 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- and Ni-containing samples). The temperature was increased to 773 K with a ramp of 8 K/min, then held for 0.5 h at 773 K. Physical mixtures of reduced Me/zeolites with Fe_2O_3 were prepared by grinding in a mortar inside a nitrogen-filled glove box. The content of Fe_2O_3 in the mixtures varied from 2.5 to 90 wt%.

The mixtures were characterized by TPR. They were studied either as prepared (further called "reduced") or after calcination. 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. TPR was carried out in a flow of 5% H₂/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. Hydrogen consumption was monitored by a thermal conductivity detector (TCD). The amount of sample was kept constant (100 mg). For TPR runs of impregnated samples 50 mg was used. The metal dispersion in metal-containing zeolites was estimated by hydrogen TPD in the range 393–873 K.

To detect metal migration, an atomic resolution analytical transmission electron microscope (ARAEM) was employed. The Hitachi HF-2000 ARAEM is a cold field emission transmission electron microscope equipped with an X-ray energy dispersive spectrometer. It is capable of forming a small probe 1 nm in diameter and of analyzing a chemical composition and crystal structure in an area larger than 1 nm. Samples after TPR to 773 K were investigated. 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 were then examined in the ARAEM with 200-keV accelerating voltage.

III. RESULTS

Reduction of Fe_2O_3 in Mixtures with Pt/Zeolite: Effect of Zeolite Structure

The reduction behavior of the Fe_2O_3 mixture with Pt/NaZSM-5 appears to be essentially the same as that observed previously for mixtures of Fe_2O_3 with Pt/NaMor (10, 11). In all cases, H₂ consumption corresponds to the reduction of hematite to magnetite. Reduced Pt/NaZSM-5 does not affect the reduction of Fe_2O_3 (Fig. 1A). In contrast, calcination of the mixture causes a dramatic shift of the TPR peak toward lower temperatures (Fig. 1, curve B). The maximum in the reduction profile is located at 555 K, whereas for Fe_2O_3 + Pt/NaMor the TPR peak is at 560 K (10).

Reduction of Fe_2O_3 Impregnated with Different Metals

The TPR profiles of Fe_2O_3 that was impregnated with Pd, Rh, Ni, or Co with a metal loading of 5.1×10^{-5} mol/g are

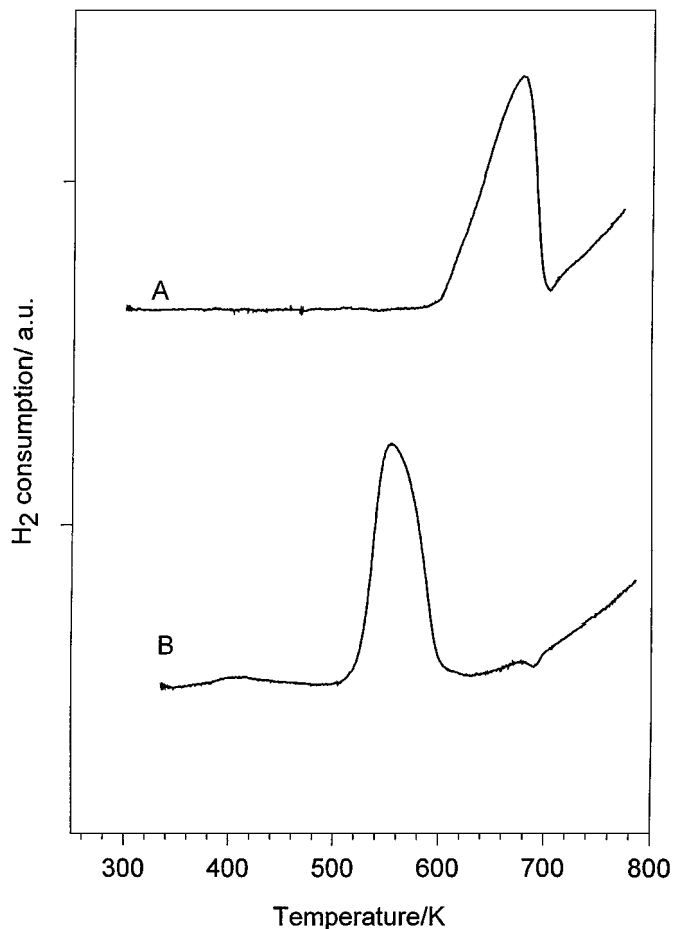


FIG. 1. TPR profiles of 1:1 Fe_2O_3 mixture with Pt/NaZSM-5: (A) mixture of Fe_2O_3 with reduced Pt/NaZSM-5; (B) calcined mixture of Fe_2O_3 with reduced Pt/NaZSM-5.

shown in Fig. 2. The presence of cobalt affects the position of the reduction peak only slightly (Fig. 2, curve B). Impregnation of Fe_2O_3 with nickel results in the appearance of a second small reduction peak in the TPR profile (Fig. 2, curve C); its maximum is located at ca. 585 K. Palladium has the same effect as platinum, described in the previous study: the reduction peak is shifted from 670 K for pure hematite to 565 K (Fig. 2, curve D). The behavior of rhodium is most surprising; it gives rise to two new peaks: one at 540 K, comparable to that for Pd and Pt, and a rather broad peak, located at 620–630 K, which is thus specific for Rh (Fig. 2, curve F). The TPR profile did not change much when the Rh content was increased to 15.3×10^{-5} mol/g (Fig. 2, curve G). For all samples, H_2 consumption is equal to the value calculated for the reduction of Fe_2O_3 to Fe_3O_4 .

The reduction profile of impregnated Fe_2O_3 clearly depends on the nature of the metal. Those that are easily reducible markedly affect the reduction of Fe_2O_3 . TPR peaks indicating reduction of platinum, palladium, and rhodium, as well as the signal characteristic of palladium hydride decomposition, were detected. These signals are very weak

because of the small amounts of metals; they are clearly visible at higher sensitivity. But even then, no signals attributable to the reduction of Co or Ni were observed.

Special experiments were carried out to estimate the surface mobility of Pt, Pd, and Rh oxides between Fe_2O_3 particles. For this purpose Me/ Fe_2O_3 samples were mixed and ground with fresh portions of hematite in different weight ratios, and the mixtures were calcined and subjected to TPR. The resulting TPR profiles are shown in Fig. 3. The profiles of Pd closely resemble those of Pt, but rhodium displays a different behavior. From mixtures of impregnated and pure Fe_2O_3 in a 1 : 1 mass ratio it is obvious that Pt and Pd are redistributed over the surface of the admixed iron oxide particles, so that only one TPR peak of enhanced reduction is present (Fig. 3, curves A and C), albeit that with platinum this peak has a broad shoulder. In mixtures with an excess of Fe_2O_3 particles, the TPR profiles consist of two peaks: one characteristic of enhanced reduction and

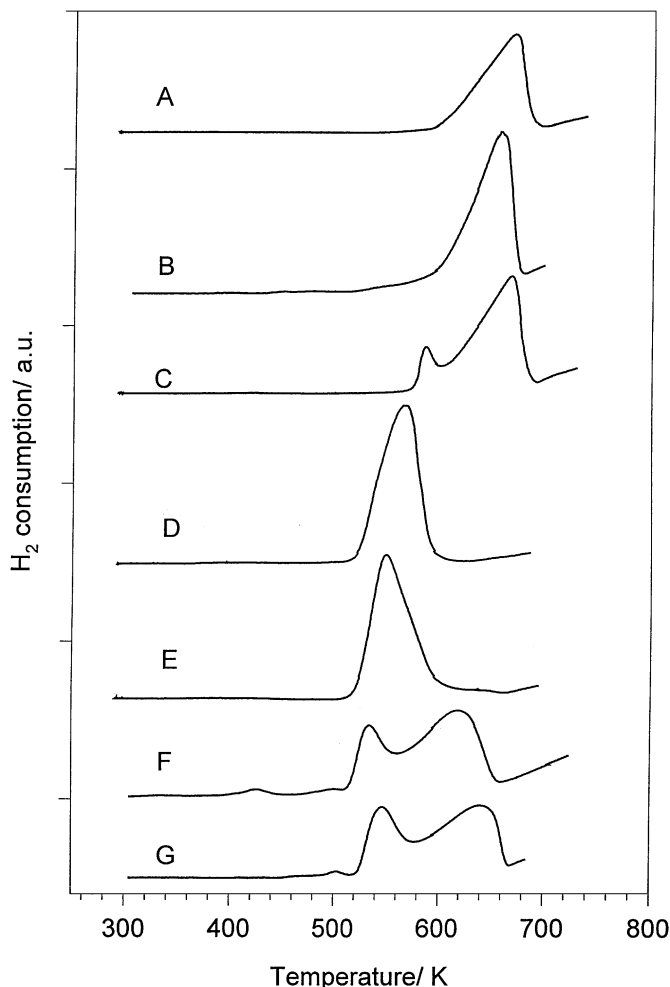


FIG. 2. TPR profiles of Fe_2O_3 impregnated with different metals: (A) pure Fe_2O_3 ; (B) Co/ Fe_2O_3 ; (C) Ni/ Fe_2O_3 ; (D) Pd/ Fe_2O_3 ; (E) Pt/ Fe_2O_3 ; (F) Rh/ Fe_2O_3 with Rh loading of 5.1×10^{-5} mol/g; (G) Rh/ Fe_2O_3 with Rh loading of 15.3×10^{-5} mol/g.

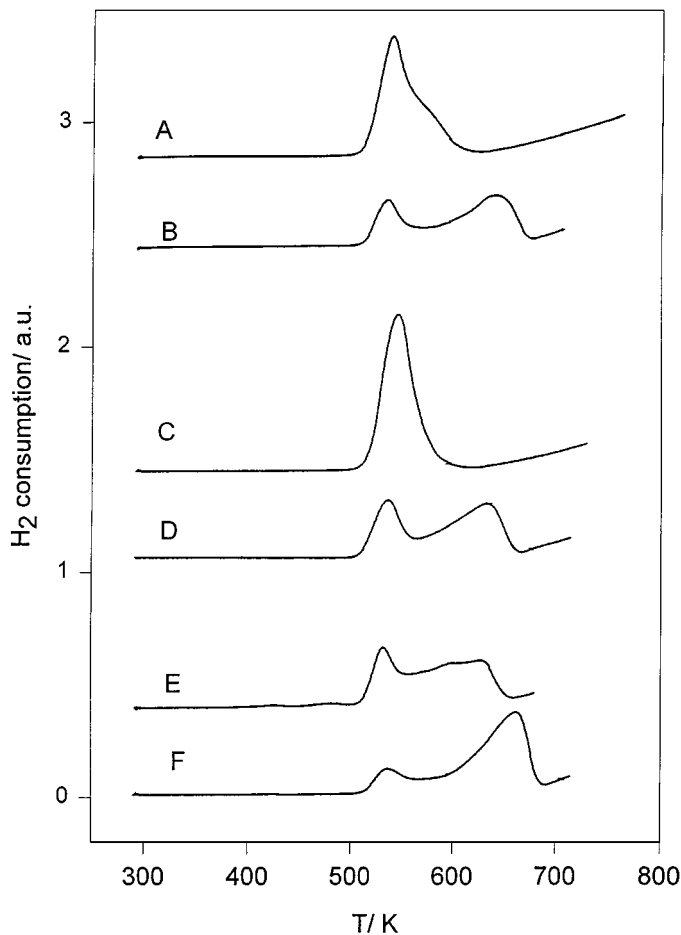


FIG. 3. TPR profiles of precalcined Me/Fe₂O₃ mixtures with fresh portions of Fe₂O₃: (A) Pt/Fe₂O₃ + Fe₂O₃, 1 : 1; (B) Pt/Fe₂O₃ + Fe₂O₃, 1 : 5; (C) Pd/Fe₂O₃ + Fe₂O₃, 1 : 1; (D) Pd/Fe₂O₃ + Fe₂O₃, 1 : 5; (E) Rh/Fe₂O₃ + Fe₂O₃, 1 : 1; (F) Rh/Fe₂O₃ + Fe₂O₃, 1 : 5.

a new broad peak with a maximum at ca. 630–640 K (Fig. 3, curves C and D); the peak area ratio is approximately 30 : 70 in both profiles. With Rh the 1 : 1 mixture of Rh/Fe₂O₃ + Fe₂O₃ (Fig. 3, curve E) resembles the 1 : 5 mixtures of Pd and Pt and the profile of the 1 : 5 Rh/Fe₂O₃ mixture with fresh Fe₂O₃ shows the same peak positions, but the reduction peak of pure hematite dominates (Fig. 3, curve F).

Reduction of Physical Mixtures of Fe₂O₃ with Me/NaZSM-5 and Me/NaMor

First experiments were carried out with mixtures containing equal amounts of Fe₂O₃ and Me/NaZSM-5 (Me = Pd, Rh, Co and Ni). For the reduced samples the TPR profiles were similar to each other (Fig. 4) and to that of pure hematite or mixtures with reduced Pt-zeolites (Fig. 1). A broad shoulder at 550–600 K in the TPR profile of the Rh-containing mixture (Fig. 4, curve D) might be caused by partial oxidation of Rh⁰, followed by migration onto Fe₂O₃. It is probable that under the glove box conditions used here,

rhodium, unlike Pt and Pd, is not preserved in the reduced state.

Completely different TPR profiles were obtained after calcination of the four systems under study (see Fig. 5). None of these profiles resembles that of the mixture of Fe₂O₃ with Pt/NaZSM-5. Neither nickel nor cobalt induced an enhanced reduction of Fe₂O₃; the TPR peaks remain at their original position (Fig. 5, curves A and B). However, the Pd-containing zeolite does enhance the reduction of a very small portion (less than 10%) of the hematite in the mixture; the TPR profile consists of two peaks located at 550 and 670 K with an area ratio of 9 : 91 (Fig. 5, curve C). The presence of rhodium leads to a rather specific TPR profile with a broad peak inbetween the two peaks with a maximum at ca. 600 K (Fig. 5, curve D).

Since the effect of Co/NaZSM-5 and Ni/NaZSM-5 on the reduction of Fe₂O₃ was negligible, no mordenite-supported samples of these metals were studied. Pd/NaMor and Rh/NaMor demonstrated the same signature as the corresponding samples with NaZSM-5. In their reduced form

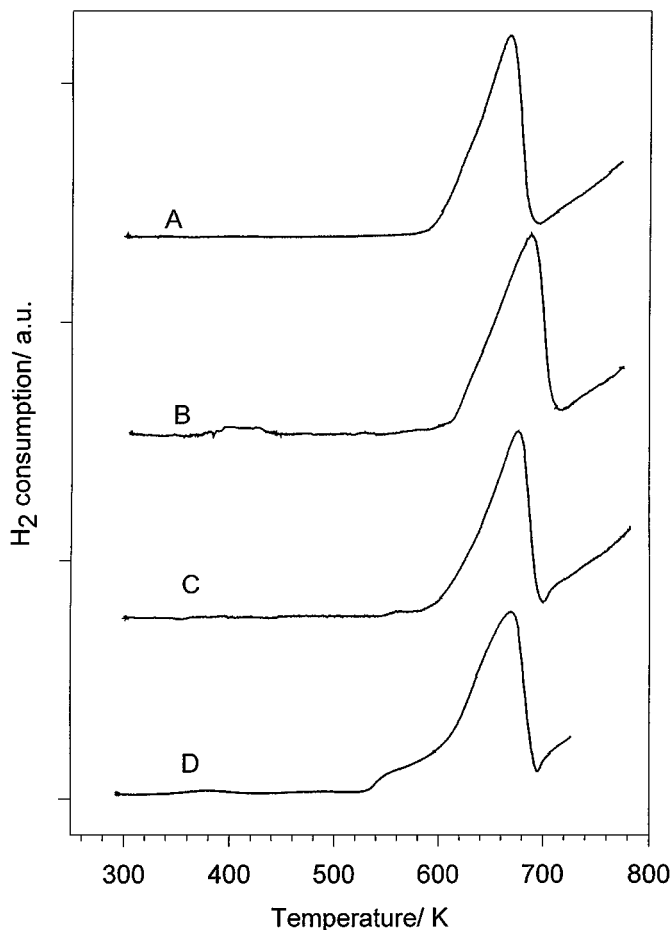


FIG. 4. TPR profiles of 1 : 1 Fe₂O₃ mixtures with reduced Me/NaZSM-5: (A) with Ni/NaZSM-5; (B) with Co/NaZSM-5; (C) with Pd/NaZSM-5; (D) with Rh/NaZSM-5.

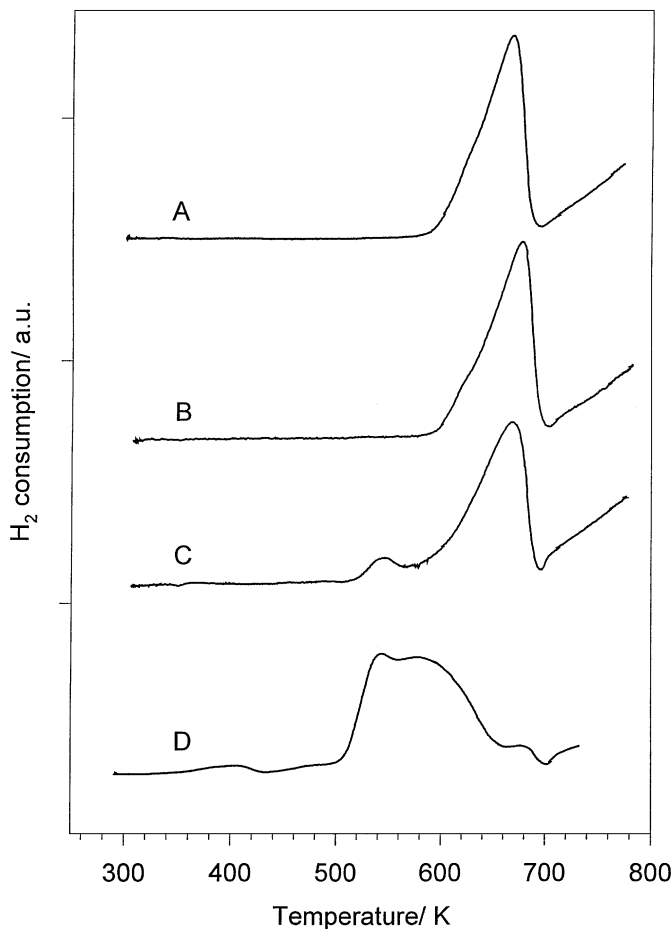


FIG. 5. TPR profiles of calcined 1:1 Fe_2O_3 mixtures with (A) Ni/NaZSM-5; (B) Co/NaZSM-5; (C) Pd/NaZSM-5; and (D) Rh/NaZSM-5.

neither Pd/NaMor nor Rh/NaMor affect the reduction of Fe_2O_3 (Fig. 6, curves A and C). The TPR profile of calcined Pd/NaMor + Fe_2O_3 (Fig. 6, curve B) looks similar to that of the mixture with Pd/NaZSM-5, the ratio of peak areas being 15 : 85. The TPR profile of the mixture Rh/NaMor + Fe_2O_3 (Fig. 6, curve D) has the broad peak typical of all calcined rhodium-containing samples. Hydrogen consumption always corresponded within 15% error to the calculated value for the transition of Fe_2O_3 to Fe_3O_4 .

Effect of Calcination Conditions on TPR Profiles

The above data show characteristic differences between Pd, Rh, and Pt. These can be attributed to the different migrational behavior of these metals. To verify this possibility, we checked whether a larger extent of enhanced reduction of iron oxide could be achieved under conditions favoring the migration of palladium and rhodium.

Standard pretreatment consisted of calcination at 773 K for 10 min. Prolonged calcination or higher temperature is expected to facilitate metal migration. Mixtures of Fe_2O_3

with Pd/NaZSM-5, Pd/NaMor, Rh/NaZSM-5, and Rh/NaMor were calcined for extended periods. The TPR profiles are shown in Figs. 7 and 8. As the results for different zeolites were essentially the same, only one representative profile is shown for each pair. After 30 min calcination the TPR profiles of Rh-containing mixtures changed significantly; the low-temperature peak became most prominent (Fig. 7). In contrast, there are only slight variations in the reduction profiles of Pd-containing mixtures after calcination for 30 min and even after 12 h (Fig. 8): the low-temperature peak is still weak and its area does not exceed 15% of the total signal. A brief calcination at 873 K has almost the same effect as extended calcination at 773 K (Fig. 8, curve D).

Effect of Mixture Composition on TPR Profiles of Fe_2O_3 Mixtures with Me/Na-Zeolite

For the above mixtures of equal amounts of iron oxide and Me/zeolite the enhancement of Fe_2O_3 reduction was incomplete. To examine whether mixtures with lower Fe_2O_3

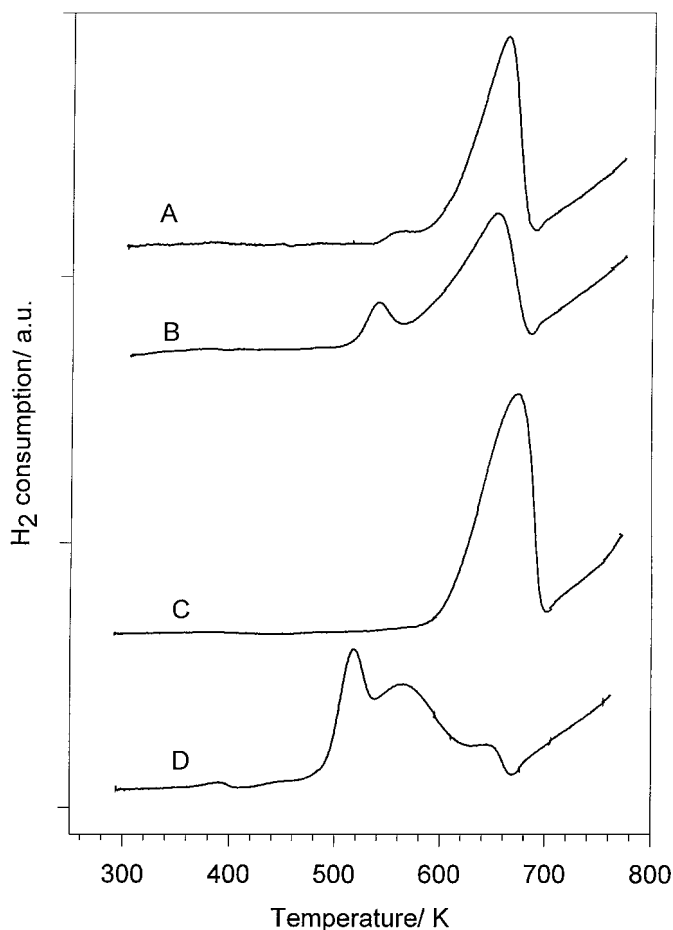


FIG. 6. TPR profiles of 1 : 1 Fe_2O_3 mixtures with Me/NaMor: (A) mixture with reduced Pd/NaMor; (B) calcined mixture with Pd/NaMor; (C) mixture with reduced Rh/NaMor; (D) calcined mixture with Rh/NaMor.

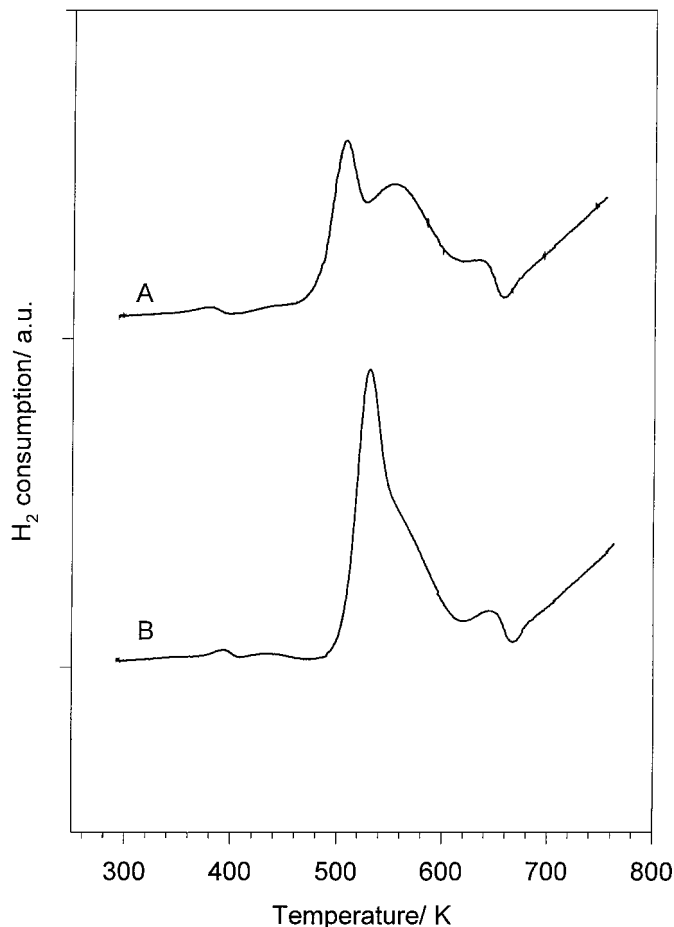


FIG. 7. Effect of calcination temperature on TPR profile of 1:1 Fe_2O_3 mixture with Rh/NaMor: (A) mixture calcined at 773 K for 10 min; (B) mixture calcined at 773 K for 30 min.

content requiring metal migration over smaller average distances display higher reduction enhancement, the Fe_2O_3 content was varied widely in some mixtures with Pd-, Rh-, and Pt-containing zeolites.

Surprisingly, it was found that for mixtures with a small Fe_2O_3 content (Me/zeolite : $\text{Fe}_2\text{O}_3 = 20 : 1$) the TPR peaks were located at lower temperatures even with prereduced Me/zeolites: 600–610 K instead of usual value 670 K. The profiles for Pt/NaZSM-5, Pd/NaZSM-5, and Rh/NaZSM-5 are shown in Fig. 9. The same TPR peak shift was observed for reduced Pt/NaMor. The presence of a peak of rhodium reduction (Fig. 9, curve C) indicates again that we did not succeed in keeping rhodium in the reduced state during preparation of the mixture. For the Pt-containing mixture the signal corresponding to platinum reduction was not detected (Fig. 9, curve A). The TPR profile of the Pd-containing mixture contains a signal corresponding to hydrogen release by palladium hydride. It cannot be excluded that in these mixtures also a small part of the Pd and Pt is oxidized, though no reduction of such oxides could be detected by TPR.

TPR profiles of calcined mixtures with different Fe_2O_3 contents are presented in Figs. 10–12. Although the three metals under study display different reduction profiles, some common features are noted in their response to increasing the iron oxide content. All the metals are capable of promoting enhanced reduction of small amounts of iron oxide; i.e., reduction peaks are situated at low temperature. In mixtures with a large excess of Fe_2O_3 two peaks exist in the TPR profiles of all metals. Even the broad “intermediate” peak, which seemed to be unique for Rh-containing samples, can be observed in mixtures with other metals when the metal/zeolite is present in excess. [See, for instance, the Pd-containing mixture with Pd/NaZSM-5 : $\text{Fe}_2\text{O}_3 = 4 : 1$ (Fig. 10, curve C).] Nevertheless, there are still some peculiarities in the behavior of every metal. For instance, with Pt/NaZSM-5 small amounts of Fe_2O_3 are reduced at very low temperatures, below 500 K (Fig. 12). For the Pd-containing mixtures such low-temperature peaks are split (Fig. 10, curves A and B).

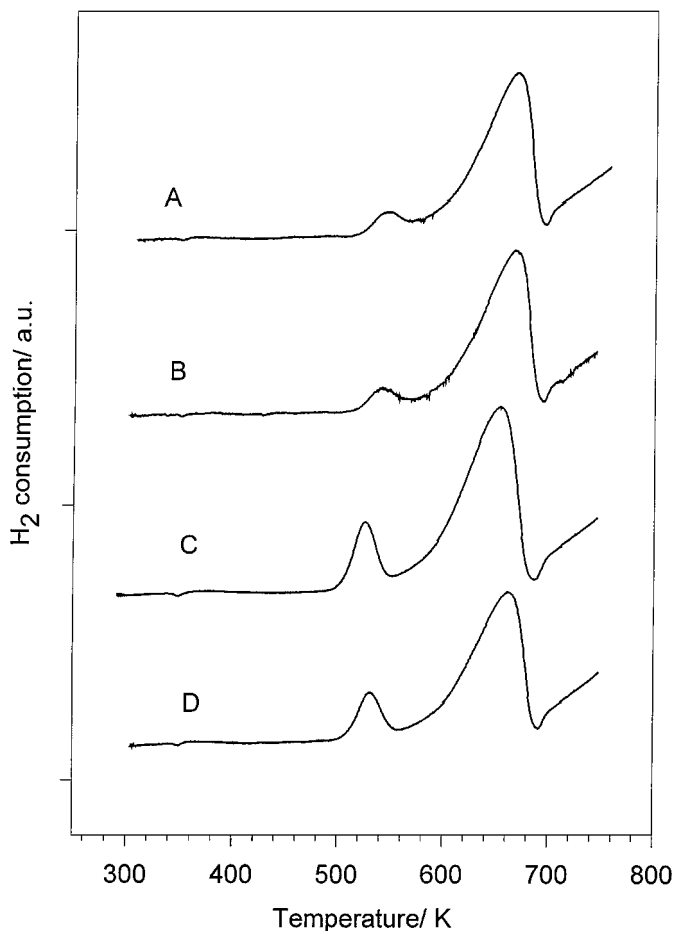


FIG. 8. Effect of calcination conditions on TPR profiles of 1:1 Fe_2O_3 mixtures with Pd/NaMor: (A) mixture calcined at 773 K for 10 min; (B) mixture calcined at 773 K for 30 min; (C) mixture calcined at 773 K for 12 h; (D) mixture calcined at 873 K for 10 min.

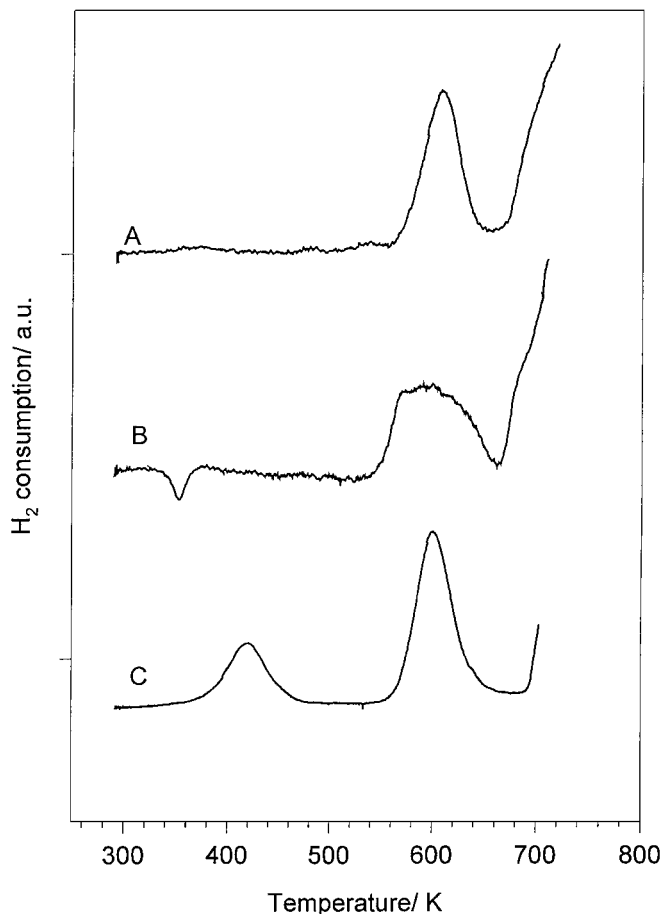


FIG. 9. Effect of low Fe_2O_3 content on TPR profiles of Fe_2O_3 mixtures with reduced Me/NaZSM-5 (weight ratio Me/NaZSM-5 : Fe_2O_3 = 20 : 1): (A) mixture with reduced Pt/NaZSM-5; (B) mixture with reduced Pd/NaZSM-5; (C) mixture with reduced Rh/NaZSM-5.

TEM and EDS of Fe_2O_3 Mixture with Rh/NaMor and Pd/NaMor

Clearly, a variety of zeolite-supported transition metals are able to induce enhanced reducibility of Fe_2O_3 . In our previous study, unambiguous EDS evidence of platinum migration out of the zeolite onto the iron oxide surface had been obtained. In the present study, the same method was applied to the 1 : 1 mixtures of Fe_2O_3 with Rh/NaMor and Pd/NaMor. Calcined mixtures subjected to TPR to 773 K were carefully examined.

TEM results show that the Fe_2O_3 particles are quite large; their sizes range from 20 to 100 nm. For a Rh-containing mixture, chemical analysis of these Fe_2O_3 particles by EDS demonstrates that both Fe and Rh signals are present; Fig. 13A shows that the Rh signal is actually more intensive than that of Fe. This spectrum along with a very weak Si peak indicates that some rhodium is no longer located inside the zeolite, but has migrated onto the iron oxide surface. Only a few large (about 20 nm in diameter) rhodium particles were found to remain inside the zeolite.

In contrast, for the Pd-containing mixture the EDS gives no evidence of palladium migration onto iron oxide. Likewise, the chemical analysis detects pure iron oxide without any traces of palladium (Fig. 13B). At the same time TEM identifies numerous well-dispersed Pd particles inside the zeolite.

Dispersion of Metal Particles in Zeolites

Metal dispersion in the initial NaZSM-5-based samples was determined by hydrogen TPD. The Pd-containing sample was found to have the highest metal dispersion, approximately 70%, compared with 45% for Pt/NaZSM-5 and 30% for Rh/NaZSM-5.

IV. DISCUSSION

The results confirm the general validity of the model that metal migration out of a zeolite onto a reducible solid is the predominant cause of enhanced reducibility in the mixtures. Though in the mixtures a few metal particles might

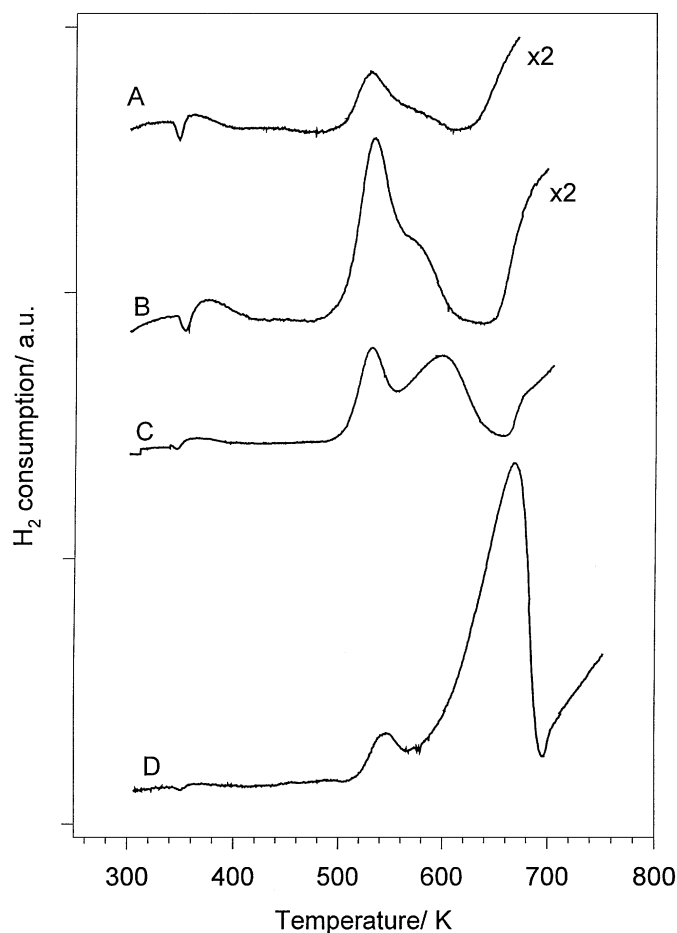


FIG. 10. Effect of mixture composition on TPR profiles of calcined Fe_2O_3 mixtures with Pd/NaZSM-5. Weight ratio Pd/NaZSM-5 : Fe_2O_3 : (A) 25 : 1; (B) 10 : 1; (C) 4 : 1; (D) 1 : 1.

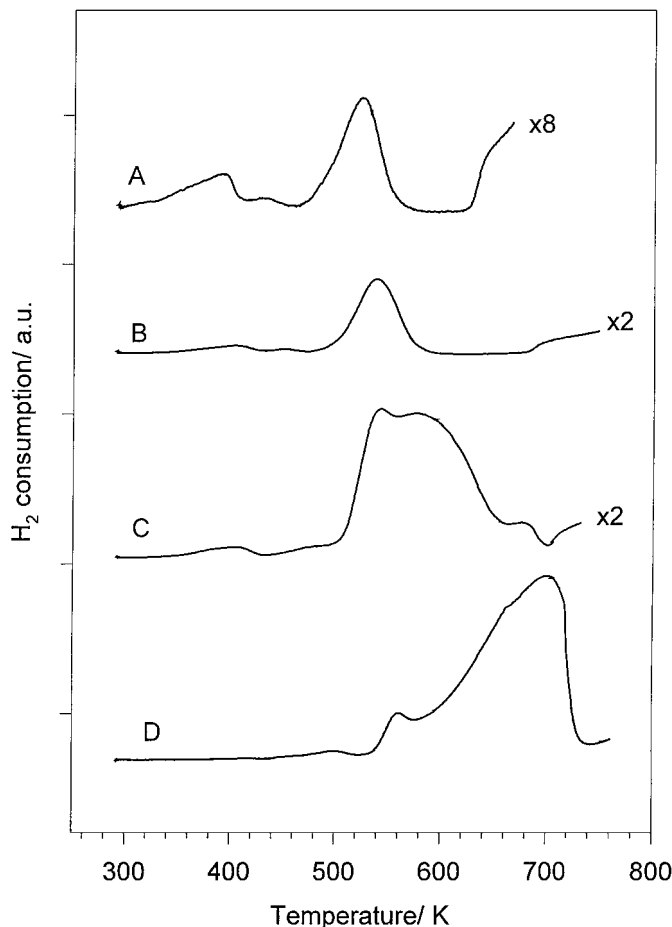


FIG. 11. Effect of mixture composition on TPR profiles of calcined Fe_2O_3 mixtures with Rh/NaZSM-5. Weight ratio Rh/NaZSM-5: Fe_2O_3 : (A) 10:1; (B) 4:1; (C) 1:1; (D) 1:10.

be located at the external surface of the zeolite crystals and thus possibly make direct contact with the hematite particles, any effect on the reducibility of such contacts is below the detection limits of the present study. The present results clearly show that reduced metal-containing zeolites do not affect the reduction of Fe_2O_3 when this oxide and the zeolite are present in comparable quantities. Formation of oxide clusters appears to be a prerequisite for the migration of a transition metal out of the zeolite resulting in enhancement of Fe_2O_3 reduction.

For mixtures of prerduced Me/zeolites with a very large excess of Fe_2O_3 an observed lowering of the reduction temperature is likely due to the presence of small amounts of oxidized metal. This follows from the appearance of the rhodium reduction peak in the TPR profile of such a mixture. Partial oxidation of Rh, which appears to be inevitable in our experimental procedure, is, however, minimal for Pt and Pd. The effect on the reducibility of traces of oxidized metals formed during mixing and grinding is negligible when comparable masses of Fe_2O_3 and zeolite are present.

The process of enhanced reduction as observed in this study is assumed to consist of the following steps:

- migration of the metal oxide(s) from zeolite onto iron oxide;
- spreading of the oxide clusters over the surface of iron oxide;
- reduction of the oxide clusters;
- hydrogen chemisorption on the metal surface;
- hydrogen transport onto the iron oxide surface (true spillover) resulting in its reduction.

The results show for each step, except for the last one, a pronounced dependence on the nature of the metal. If any step is slow or requires a very high temperature, no enhanced reduction is observed. This appears to be the case for Co- and Ni-containing samples; even if Co and Ni species are able to migrate out of the zeolite onto iron oxide, they are not reduced at a lower temperature than Fe_2O_3 , as follows from the results obtained with impregnated samples. In contrast, Pt, Pd, and Rh are reduced at temperatures

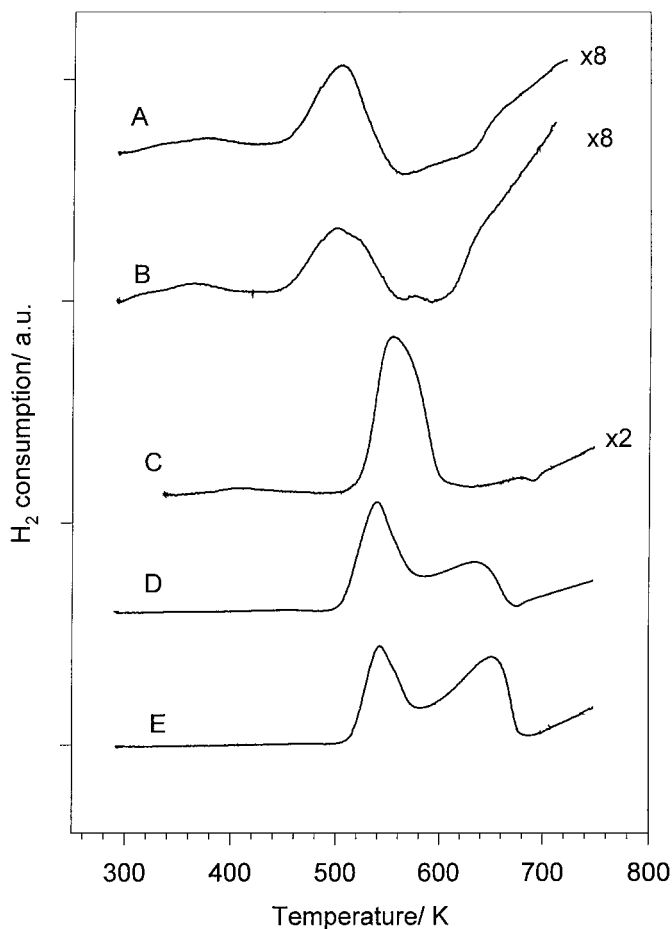


FIG. 12. Effect of mixture composition on TPR profiles of calcined Fe_2O_3 mixtures with Pt/NaZSM-5. Weight ratio Pt/NaZSM-5: Fe_2O_3 : (A) 25:1; (B) 20:1; (C) 1:1; (D) 1:4; (E) 1:10.

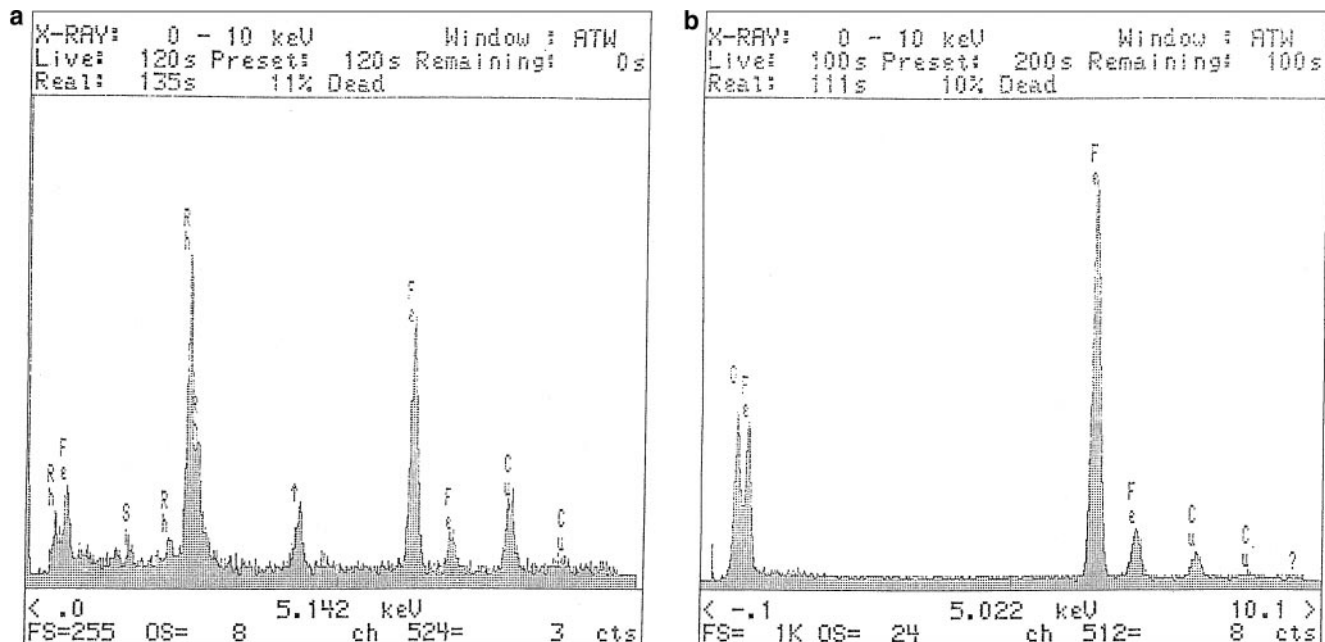


FIG. 13. X-Ray energy dispersive spectra of calcined and subsequently reduced Fe_2O_3 mixtures with (A) Rh/NaMor and (B) Pd/NaMor.

low enough to promote enhanced reduction of iron oxide, provided that they are in direct contact with it. However, the extent of this enhancement depends on a number of factors which will be inspected below.

First, mere geometric effects should be discussed: one can imagine that the number of metal-containing particles in contact with iron oxide is insufficient if the metal particles are poorly dispersed. Dispersion of the metals in the initial samples was found highest for Pd in NaZSM-5 (70%). It follows that for Pd one condition was fulfilled to be transformed into small oxide clusters. Dispersion is evidently not the cause of the poor ability of Pd to enhance Fe_2O_3 reduction. However EDS-TEM analysis could not detect any Pd on the Fe_2O_3 , whereas the same method did identify rhodium and, in the previous study, platinum on the iron oxide surface. Two additional facts indicate that in the physical mixtures where no reduction enhancement was observed no Pd had migrated onto the Fe_2O_3 : (1) the high reducibility enhancement found for Fe_2O_3 , onto which Pd was directly impregnated, and (2) the high ability of palladium to spread over the fresh Fe_2O_3 portion admixed to Pd/ Fe_2O_3 . It thus follows that Pd oxide clusters do not migrate through zeolite channels under conditions where platinum oxide clusters are highly mobile.

The migration of oxides over the surface of another oxide has been studied by Xie *et al.* (13) and Knözinger and Taglauer (14). From the formation of monolayers observed by these authors it follows that the Gibbs free energy of the interface is lower than the surface free energy of the supporting oxide. This provides the driving force for the migration of oxide clusters onto hematite particles observed in

the present work. The results of Xie *et al.* also signal a general trend for the relative mobility: low-melting-point compounds usually migrate at lower temperatures than high-melting-point compounds. This trend provides a possible clue for the different behavior of Pt and Pd in the present work. Platinum is known to form two oxides, PtO and PtO₂. The former decomposes at 823 K; the latter has a low melting point of 723 K (15), which is even below the calcination temperature used in the present work. In contrast, no PdO₂ is known and the melting point of PdO, the only stable palladium oxide, is much higher (1143 K). We thus conclude that the low mobility of PdO is the most likely cause for the absence of its migration out of the zeolite.

The behavior of rhodium is more complex. Unlike Pd, its oxide can migrate and its arrival on the Fe_2O_3 surface has been detected by EDS. However, only with rhodium-containing systems is a third broad TPR peak at ca. 570 K observed along with the peaks of unaffected and promoted Fe_2O_3 . This peak is present even in the profile of Fe_2O_3 impregnated with rhodium. In comparison to platinum, the migration of rhodium oxides seems to be slower. As a consequence the extent of migration strongly depends on the duration of the calcination treatment for Rh, but not for Pd (Fig. 7). It is interesting to note that long-term calcination leads to a decrease in the broad peak. Considering that rhodium has been detected on Fe_2O_3 particles, we assume that rhodium oxides are able to migrate out of the zeolite, but their spreading over iron oxide is difficult. The observations with the Rh/ Fe_2O_3 + Fe_2O_3 mixtures in Fig. 3 support this assumption. It is further supported by the phase diagram of the Rh-O₂ system (16) and our previous

observation that RhO_2 and Rh_2O_3 are formed in zeolites such as NaY (17). For Rh_2O_3 it might be important that it is isomorphous with Fe_2O_3 (16). This sets the scene for a very specific interaction between both oxides. Indeed, the broad reduction peak in the TPR profiles of the Rh-containing samples indicates that such an interaction exists. We do not, however, exclude, that traces of Rh chloride might have survived the oxidation/reduction treatment. It is well known that RhCl_3 is highly mobile and volatile.

CONCLUSIONS

Under oxidizing conditions, transition metals can migrate out of zeolites onto the surface of an admixed oxide. Under these conditions, no migration of the reduced metals can be observed. In the Na form of zeolites the predominant migrating species are metal oxide clusters. The mobility of oxides is different for Pt, Pd, and Rh. Platinum dioxide readily migrates through zeolite channels onto iron oxide and further over this oxide. This high mobility is in accordance with the low melting point of PtO_2 . Palladium oxide (PdO), which is known to have a very high melting point, is least capable of migrating through zeolite channels, even if its initial dispersion is quite high. Rhodium oxide clusters migrate out of the zeolite, but on the surface of iron oxide they are less mobile, indicating strong chemical interaction of both oxides.

Once a transition metal oxide has migrated onto Fe_2O_3 , it can be reduced. If this occurs at low temperature, as with Pt, Pd, or Rh, the reduced metal particles are able to dissociate H_2 and thus to promote the reduction of Fe_2O_3 . The presence of the reduced metal in direct contact with Fe_2O_3 appears to be a prerequisite for significant reduction en-

hancement of Fe_2O_3 . For metal particles inside a zeolite no hydrogen spillover through zeolite channels has been detected.

ACKNOWLEDGMENT

Financial support of this research by the National Science Foundation through Contract CTS-9629963 is gratefully acknowledged.

REFERENCES

1. Hegedüs, A. J., Millner, T., Neugebauer, J., and Sasvári, K., *Z. Anorg. Chem.* **281**, 64 (1955).
2. Verhoeven, W., and Delmon, B., *C. R. Acad. Sci. Ser. C* **262**, 33 (1966).
3. Il'chenko, N. I., *Kinet. Katal.* **8**, 184 (1967).
4. Batley, G. E., Ekstrom, A., and Johnson, D. A., *J. Catal.* **34**, 368 (1974).
5. Hurst, N. W., Gentry, S. J., Jones, A., and McNicol, B. D., *Catal. Rev. Sci. Eng.* **24**, 233 (1982).
6. Il'chenko, N. I., *Russ. Chem. Rev.* **41**, 47 (1972).
7. Conner, W. C., Teichner, S. J., and Pajonk, G. M., *Adv. Catal.* **34**, 1 (1986).
8. Conner, W. C., and Falconer, J. L., *Chem. Rev.* **95**, 759 (1995).
9. Boudart, M., *Adv. Catal.* **20**, 153 (1969).
10. Fröhlich, G., and Sachtler, W. M. H., *J. Chem. Soc. Faraday Trans.* **94**, 1339 (1998).
11. Liu, H.-Y., Chiou, W.-A., Fröhlich, G., and Sachtler, W. M. H., *Topics in Catal.*, (in press).
12. Brown, R., Cooper, M. E., and Whan, D. A., *Appl. Catal.* **3**, 177 (1982).
13. Xie, Y. Ch., and Tang, Y. Q., *Adv. Catal.* **37**, 1 (1990).
14. Knözinger, H., and Taglauer, E., in "Catalysis" (J. J. Spivey, Ed.), Vol. 10, p. 1. Roy. Soc. Chem., Cambridge, 1993.
15. Lide, D. R., and Frederikse, H. P. R. (Eds.), "Handbook of Chemistry and Physics." CRC Press, Boca Raton, FL, 1993-1994.
16. Muller, O., and Roy, R., *J. Less-Common Met.* **16**, 129 (1968).
17. Schünemann, V., Adelman, B., and Sachtler, W. M. H., *Catal. Lett.* **27**, 259 (1994).
18. "Gmelin Handbook of Inorganic Chemistry," Rh. Suppl. V. B1, p. 39. Springer-Verlag, Berlin/New York, 1982.