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A Model of Metal–Oxide Support Interaction for Rh on TiO_2

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Using the Rh/TiO_2 catalyst system, a simple model for the different kinds of interaction that occur following a low- and a high-temperature reduction of Group VIII noble metals supported on TiO_2, was developed. The model proposes a delocalized transfer of charge from Rh to TiO_2 after low-temperature reduction and a localized (chemical bonding) transfer of charge from the support to Rh after a high-temperature reduction. In addition, it is suggested that migration of a reduced species of the support is responsible, in part, for the depression of hydrogenolysis activity following a high-temperature reduction. The experimental evidences for the latter comes from comparing H_2 and H atom reduction, the kinetics of the onset of strong-metal-support interaction, and a strong analogy between group VIII–group Ib and group VIII–TiO_2 interaction effects on structure-sensitive and insensitive reactions. The kind of charge transfer is based on observed effects on kinetic parameters and previously reported spectroscopic experiments.

I. INTRODUCTION

The concept of "synergetic promotion" by the support, introduced by Schwab more than 50 years ago (*1*) to describe changes in activation energy of some reactions on supported catalysts, was the forerunner of what today is known as "metal-support interaction." In the last few years considerable effort has been directed toward elucidation of the interaction between Group VIII metals and titanium dioxide. This kind of interaction has been characterized by the acronym SMSI, standing for strong-metal-support interaction (*2*). However, it may also be used, as has been suggested by Boudart (*3*), with the meaning Schwab-metal-support interaction in recognition of Schwab's pioneering work. It is generally accepted that the extent of SMSI depends on the reducibility of the support (*4*). That an electron transfer from the TiO_2 to the Group VIII metal accompanies a high-temperature reduction has also been widely reported (*5*), but there exist at least two X-ray photoelectron spectroscopy (XPS) investigations of Pt/TiO_2 that find either no correlation between binding energy and chemisorption effects (*6*) or no measurable shifts (*7*). Moreover, Santos and Dumesic have presented a convincing argument for charge transfer from Fe to TiO_2 based on ammonia synthesis activity after a high-temperature reduction (*8*). Presuming that an electron transfer between metal particle and TiO_2 does occur, the crucial point to be clarified is whether it is a cooperative electronic interaction or a localized interaction or, indeed, whether the electron transfer directly affects catalysis. Tauster *et al.* (*2a*) have explained SMSI in terms of a localized strong bonding between the Ti cation and the noble metal. Meriadeau *et al.* on the other hand have pictured a mechanism involving collective properties of electrons (n-type semiconductivity) in reduced TiO_2 (*9*), in which the difference in Fermi levels is the driving force for the electron transfer. This model is very similar to that originally proposed by Schwab (*10*).

An argument against an electron transfer effect on catalysis has been presented by Ponec (*11*), who points out that a 2-nm particle, e.g., Pd, has about 10^3 delocalized electrons and asks why then a transfer of something of the order of one electron into

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a sea of a thousand should have a large effect on catalysis? Put another way, theoretical estimates of the screening length of a one-electron charge suggest that 76% of the charge would be screened by this mobile sea of electrons over about one-fourth of the nearest-neighbor distance for Cu (*12*), and the result cannot be too different for other metals. Moreover, an electron transfer would be expected to result in a change in the activation energy while, as will be discussed below, the dominant change in all reactions we have tested over Rh/TiO_2, after reduction at high temperature, involve changes in the frequency factor with about constant activation energies.

We have recently studied the effect of the degree of percentage exposed (metal dispersion) in a series of Rh/TiO_2 catalysts (*13*). Our results indicate that the interaction is more pronounced on the well-dispersed catalysts. The activity for the hydrogenolysis of ethane and n-butane after reduction at 773°K (high-temperature reduction—HTR) decreases with increasing percentage exposed showing a greater extent of interaction for the smaller particles. Following reduction at 473 or 523°K (low-temperature reduction—LTR) the opposite trend is observed: the activity increases with the percentage exposed. The difference between the ethane hydrogenolysis rates of low- and high-temperature reduced catalysts is several orders of magnitude at all dispersions.

The present work develops the rudiments of a model for this metal-support interaction which accounts for the observed behavior as a function of percentage exposed. It considers specific Rh-TiO_2 interactions after both the LTR and HTR. Both interactions involve electron transfer, but a critical aspect of the proposed model invokes migration of a species originating from the support over the surface of the metal particles. It is proposed that for the HTR case the electron transfer is from the support to the metal and it is localized at the metal–oxide interface. For LTR the charge is transferred from the metal to the support and the charge deficiency is delocalized over the whole metal particle.

2. EXPERIMENTAL

The same catalysts discussed in Ref. (*13*) were used. These catalysts were prepared by incipient wetness impregnation of TiO_2 (Degussa P25, 50 ± 15 m^2/g) with a solution of $Rh(NO_3)_3$ to obtain 2 wt% Rh. The catalysts were first dried for 2 days in air at room temperature, then 3 h at 383°K in air, reduced at 773°K in flowing H_2 for 2 h, oxidized at 673°K in flowing O_2 for 2 h, and then stored. Subsequent low-temperature (523°K) and high-temperature (773°K) reductions were carried out *in situ* for 3 h before activity or chemisorption measurements were performed. In every case, purified H_2 diffused through a palladium–silver cell was used.

Apple *et al.* indicate that the percentage exposed depends on the pH of the impregnating solution (*14*). Therefore, in order to get different percentages exposed, the pH of the impregnating solution was systematically varied. A range of catalyst percentage exposed from 33 to 76% was obtained. It was demonstrated that there exists a pH optimum at about 8.5, which results in the highest percentage exposed.

To obtain a percentage exposed higher than 76%, one catalyst was prepared by an ion-exchange procedure. The TiO_2 was first immersed in NH_4OH solution at pH = 11 for 15 h. It was then washed with distilled water until a pH = 7.5 was obtained, then filtered. Subsequently, the ion exchange was allowed to occur by placing the filtered product in a 0.01 M $Rh(NO_3)_3$ solution (0.01 g TiO_2/cm^3 solution) for 15 h. The product was filtered and washed with distilled water and then with pure methanol to remove water. Finally, the same drying and reduction procedure used for impregnated catalysts was followed. The Rh loading, measured by atomic absorption of HCl-extracted Rh, was 0.3% and the percentage exposed was

100% measured by hydrogen chemisorption at room temperature.

Hydrogen chemisorption was carried out in a conventional Pyrex volumetric adsorption system equipped with a Baratron MKS 0–1000 Torr precision pressure gauge. The percentage exposed was calculated assuming a hydrogen atom to Rh ratio of 1 using the quantity adsorbed at room temperature measured by extrapolating the isotherm to zero pressure. The catalytic activities were measured in a differential flow reactor and a pulse reactor. A catalyst weight of 0.1 g was used in a packed bed 1.0-cm long preceded by a preheater section of 80–100 mesh glass beads that had been washed with sulfuric–chromic acid solution and heated to high temperature in air. The reaction temperature was monitored by an iron-constantan thermocouple in contact with the catalyst bed. For the pulse reactor H_2 was used as carrier gas in which a 0.05-cm^3 pulse of hydrocarbon was injected. For the flow reactor partial pressures of hydrogen and ethane were varied from 70 to 700 Torr, using pure He as diluent. High-purity ethane (99.96% min.) obtained from Matheson Company and CP grade n-butane were used. The products were analyzed by gas chromatography.

Two types of reduction were performed (i) the standard reduction by flowing hydrogen at 1 atm at 473 or 773°K for 3 h through the reactor catalyst bed and (ii) H atoms produced by a microwave discharge at 2 Torr total pressure and room temperature. The microwave power generator was a Scintillonics, Inc. Model HV15A. A very thin layer of catalyst was placed on a fritted disk in a Pyrex tube, passing through the microwave cavity, which was located 10 cm above the catalyst. In every case the hydrogen used was purified by diffusing through a palladium–silver cell.

3. RESULTS AND DISCUSSION

3.1 Effect of Percentage Exposed on Rates

Since the original work by Tauster *et al.* (*2a*), investigators working with noble metals supported on TiO_2 have been struggling with the problem of how to report rates on catalysts following a high-temperature reduction. That is, by convention we report turnover frequencies or specific rates per unit metal area based on a site density or metal area, respectively, measured by hydrogen (or sometimes CO) chemisorption. However, the chemisorption property is altered or entirely lost in the presence of SMSI, making it an unreliable measure of metal site density.

Electron microscopy indicates that Pt is more resistant to sintering when supported on TiO_2 than when supported on Al_2O_3, SiO_2, or C (*15*), and a recent transmission electron microscopy investigation of Ir/TiO_2 could not detect noticeable sintering after 773°K reduction, even for a catalyst which apparently had 100% exposed (*16*). Thus, common practice has been to report rates on TiO_2-supported catalysts reduced at high temperature based on percentage exposed measured on the same catalyst after a low-temperature reduction. We follow this procedure but take the added precaution of initially cycling the catalyst through a high-temperature reduction (HTR) at 773°K and an oxidation at 673°K before measuring the percentage exposed by H_2 chemisorption following a low-temperature reduction (LTR) at 523°K. We do this because both our X-ray photoelectron results (*5b*) and H_2 chemisorption indicate some sintering following the initial HTR, but a reproducible particle size thereafter.

We have sought additional reactivity justification for the presumption that the site density following LTR is a reasonable measure of site density following HTR. First, it is noted that when a structure-insensitive reaction such as cyclohexane dehydrogenation is considered, there is only a weak dependence of the activity on the temperature of reduction, e.g., never more than a factor of 2 depression in the rate after HTR relative to LTR (*13*). This is a negligible change compared to the 2 to 5 orders of magnitude (depending on reactant) depression of hydrogenolysis activity. Thus, one might normalize the rates of a structure-sensitive reaction (hydrogenolysis) to a structure-insensitive reaction (dehydrogenation) since these can be measured for both reactions after LTR or HTR. This appears to be no less arbitrary than assuming that the percentage exposed measured by H_2 chemisorption following LTR applies following HTR. In order to estimate the quality of the latter assumption the activity of a catalyst of very different loading was compared to the standard series of 2% Rh catalysts prepared by impregnation with percentages exposed between 33 and 76%. It was reasoned that if a substantial change in percentage exposed accompanies HTR, then a catalyst of very low loading (0.3%), very high percentage exposed (100%), and prepared by a different method (ion exchange) would be unlikely to fit onto the activity versus percentage exposed curve observed for the impregnated catalysts. However, the activity curve measured between 33 and 76% extrapolated to 100% exposed predicts the activity of this low loading catalyst very well (*13*). We therefore draw from our activity test the same conclusion as Foger (*16*) has from electron microscopy, i.e., there is no noticeable sintering after HTR relative to LTR.

Ethane and n-butane hydrogenolysis rates after HTR were normalized to the rate on the catalyst of lowest percentage exposed and are shown in Fig. 1 as a function of percentage exposed. As indicated above, these rates decrease as percentage exposed increases. Therefore, in looking for a correlation of activity with a property of the metal–oxide interface we can expect the activity to be inversely proportional to the metal–oxide contact area, curve (a), which might be expected if the interaction were delocalized, or inversely proportional to the perimeter of the metal particles, curve (b), which might be expected if the interaction is localized and only apparent for that part of the metal–oxide interface exposed to the gas phase. Both curves were calculated assuming hemispherical particles. However, because the rates were normalized to the lowest dispersed catalyst, parameters of geometric shape will cancel. Clearly the data fit curve (b) much better, suggesting that the interaction after HTR occurs locally at the metal–oxide interface, and only those atoms exposed around the perimeter of the particle appear to be affected (rendered inactive).

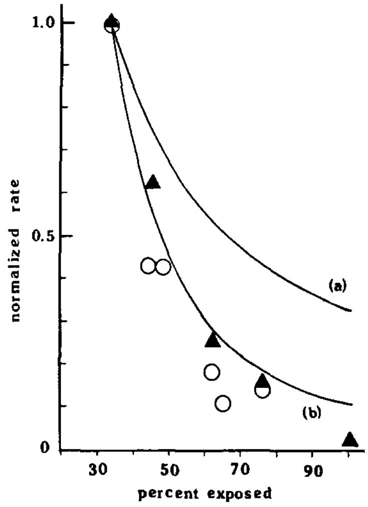

FIG. 1. Normalized rates for ethane (circles) and n-butane (triangles) hydrogenolysis after high-temperature reduction (773°K) as a function of percentage exposed. (a) Inverse of normalized metal area. (b) Inverse of normalized particle perimeter.

It is interesting to note the slight systematic departure of the data from curve (b) to lower values as the percentage exposed increases. This is consistent with the observed spreading of the small metal particles over the support observed by electron microscopy after reduction at 773°K for several Group VIII noble metals supported on TiO_2 (*15*), which would enlarge the perimeter of the particles, resulting in a larger effect at high percentage exposed than that predicted by using the original average particle size. It must be recalled that the percentage exposed was measured after LTR and, as discussed above, was assumed to be unchanged by the HTR. Note also the implication that there exists a slight reversible morphology change that accompanies SMSI as distinct from the irreversible sintering that accompanies the initial HTR.

Figure 2 shows that unlike the rates after HTR, the normalized rates after LTR fit better the curve representing the normalized metal–oxide contact area (or exposed metal area). This indicates that the interaction occurring at low temperatures is different in nature from that observed after HTR, and probably involves a delocalized electron transfer resulting from the difference in the work functions of the metal and the support. Undoped stoichiometric TiO_2 has a work function of 6.2 eV (*17*), while the work function of Rh is 4.98 eV (*18*) indicating that the equilibrium of the Fermi level at the interface would cause electron transfer from the metal to the support. The transfer after HTR may be in the opposite direction since reduced TiO_2 has a work function of 4.6 eV (*19*).

3.2 *Effect of SMSI on Kinetic Parameters*

The variation of activation energy and orders of reaction with temperature of reduction were studied for the hydrogenolysis of ethane over a Rh/TiO_2 catalyst series with different Rh percentage exposed. Figure 3 shows the apparent activation energies for the different catalysts as a function of percentage exposed. After LTR the activation energy decreases with increasing metal percentage exposed, but after HTR it is essentially constant within the range of percentage exposed considered. It is remarkable that this value of 197 kJ/mol coincides with that obtained for the catalyst of lowest percentage exposed after LTR. This fact suggests that some of the particles are not affected by the interaction and retain the properties of bulk Rh metal (large particles).

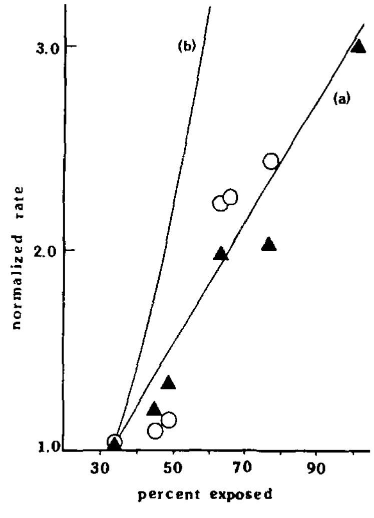

FIG. 2. Normalized rates for ethane (circles) and n-butane (triangles) hydrogenolysis after low-temperature reduction (523°K) as a function of percentage exposed. (a) Normalized metal area. (b) Normalized particle perimeter.

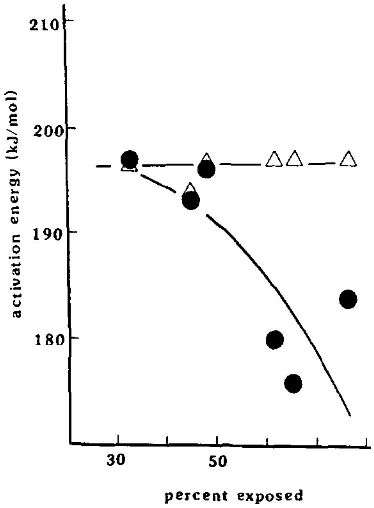

FIG. 3. Activation energies for ethane hydrogenolysis after low-temperature reduction (circles) and high-temperature reduction (triangles) as a function of percentage exposed.

The decrease in activation energy after LTR for the catalyst of high percentage exposed indicates a different kind of interaction, which can be pictured in terms of a delocalized transfer of electrons. The Fermi level of metals lies generally higher than that of semiconductors, so it may be expected that in the first stage of reduction electrons will flow from the Rh to the TiO_2. This interpretation was first given by Schwab (*10*), who correlated changes in activation energy with collective properties of the semiconductor (n-type or p-type). Accordingly, the activation energy for a donor reaction would decrease when charge is transferred from the metal to the support. In the case of ethane hydrogenolysis, a depletion of the free electron density in the metal may favor the stabilization of the C_2H_x intermediate of the hydrogenolysis reaction, weakening the C–C bond and causing a decrease in the activation energy.

The orders in hydrogen were observed to change after reduction at 773°K compared to the orders obtained after reduction at low temperatures, while the orders in ethane pressure remain nearly constant. These changes in pressure dependance are very similar to the changes observed when Group VIII metals are alloyed with Group Ib metals. In Table 1 a comparison between our data and those reported in Ref. (*20*) has been made. We want to stress the similarity of the effects of SMSI after HTR and the Group VIII–Group Ib alloying because the latter is believed to be a clear example of localized interaction (*21*) where some active sites are deactivated while the rest retain their original capabilities.

3.3 The Analogy Between Group VIII–Group Ib and Group VIII–TiO_2 Interaction

To emphasize the analogy between the deactivation of a Group VIII metal by addition of a Group Ib metal and the deactivation of a Group VIII metal by the degree of interaction with TiO_2, we make a direct comparison for two reactions in Fig. 4. The degree of metal–metal interaction is changed by varying the Cu/Ni ratio while the metal–oxide interaction is changed by varying the extent of reduction (temperature of reduction for a fixed period of 2 h). In both cases the activity of the Group VIII metal is affected only modestly for the structure-insensitive reaction, cyclohexane dehydrogenation, but the structure-sensitive reaction, hydrogenolysis, is depressed by orders of magnitude. Similar behavior has also been reported for the Ru–Cu system by Sinfelt (*22*).

TABLE 1

Catalyst	Ethane order	Hydrogen order
Rh/TiO_2 catalysts		
H/M = 76% (LTR)	1.0	−2.3
H/M = 76% (HTR)	1.0	−1.6
H/M = 33% (LTR)	1.1	−2.2
H/M = 33% (HTR)	1.0	−1.6
Ni–Cu catalysts[a]		
Unsupported Ni	0.9	−2.1
Ni–Cu (6% Cu)	0.8	−1.3
Ni–Cu (60% Cu)	0.8	−1.2

[a] Ref. (*20*).

Further evidence of the similarity between Group VIII–Group Ib alloys and SMSI appears in the comparison of other hydrocarbon reactions. For example, it has been reported (*23*) that for SiO_2-supported bimetallic Pt–Au catalysts with low Pt content (Pt/Au = 0.03) the isomerization of hexane occurs via the bond-shift (C_3 metallocycle) mechanism in preference to the cyclic (C_5 metallocycle) mechanism. On the other hand, at high Pt contents the cyclic mechanism was dominant. The low Pt content catalysts were inactive for ring opening of methylcyclopentane, a necessary step in isomerization through the C_5 metallocycle mechanism. Clarke *et al.* (*24*), have also observed this clear switch in isomerization mechanism when the ratio Pt/Au is very low, i.e., isomerization occurs almost entirely by the C_3 metallocycle mechanism and the methylcyclopentane ring is not opened. Analogously, Dauscher *et al.* (*25*) studying the SMSI have found that highly dispersed 0.25 wt% (pure) Pt on TiO_2, after reduction at 673°K, showed a drastic reduction in the C_5 metallocycle mechanism, as in the case of bimetallic catalysts.

3.4 Reduction by H atoms

After reduction by H atoms at room temperature the H_2 chemisorption capability and hydrogenolysis activity were measured

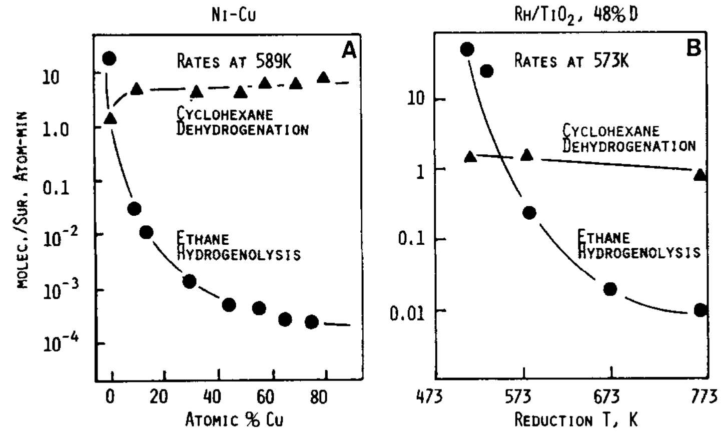

FIG. 4. Ethane hydrogenolysis and cyclohexane dehydrogenation on (a) Ni–Cu catalysts as a function of Cu content, and (b) Rh/TiO_2 catalyst as a function of reduction temperature.

and compared to the values obtained after standard reductions. The results are shown in Table 2. They are substantially the same as those obtained after LTR.

It has been shown that H atoms produced by microwave discharge are able to reduce TiO_2 at low temperatures. After exposure to H atoms, for 3 min at 77°K, an EPR signal due to Ti^{3+} is observed and it does not disappear after exposure to oxygen. This fact has lead Che *et al.* to the conclusion that Ti^{3+} species are below the surface (*26*). However, UPS, ELS, and angle-resolved XPS measurements have shown that when Ti^{3+}/O^{2-} vacancies are created on the surface at room temperature by ion bombardment it is necessary to anneal the TiO_2 crystal at temperatures as high as 673°K to allow the O^{2-} ions to diffuse up from the bulk effectively transporting Ti^{3+} species below the surface (*27*). Therefore, it seems unlikely that reduction by H atoms at low temperatures would not produce Ti^{3+} on the surface. In any case, our results prove that the Rh/TiO_2 interaction following HTR cannot be due to the collective properties of the reduced TiO_2 because the creation of Ti^{3+}/O^{2-} vacancies (either on the surface or in the bulk) causes an increase in the n-type conductivity which, according to Ref. (*9*), would induce a suppression in hydrogen chemisorption and catalytic activity. No such effect was detected in either of the two experiments using hydrogen atoms reduction.

TABLE 2

Reduction	Rate (molec./surf.Rh at.min) (n-butane hydrogenolysis at 473°K)	H/Rh
LTR	20	0.45
HTR	0.0009	0.04
H atoms (room temp) + LTR	15	—
H atoms (room temp) + 773°K (vacuum)	9	0.40

A Ti^{3+}/lattice oxide vacancy must be created close to the metal particle and, in addition, metal atoms must have the necessary mobility to get to the O^{2-} vacancy and form the kind of bonding described theoretically by Horsley (*5c*). We have tried to perform separately the two steps by first creating the O^{2-} vacancy by bombarding the catalyst with H atoms at room temperature and then increasing the temperature in vacuum to induce the movement of Rh atoms (particles). However, as shown in Table 2 no significant effect was observed. This may be due to O^{2-} ions diffusing from the bulk and occupying the Ti^{3+}/O^{2-} vacancies before any

Rh atom (particle) can reach them. Therefore, it appears necessary to have present both reduction by H atoms and high-temperature mobility simultaneously, so the Rh atoms (particles) can move into the O^{2-} vacancy before another O ion can occupy it.

The above discussion presumes that metal atoms or particles must move to lattice oxide vacancies formed by the surface reduction of Ti^{4+} to Ti^{3+}, i.e., that the interaction following HTR resulting in hydrogenolysis deactivation is primarily electronic. However, the constant activation energy independent of the degree of hydrogenolysis activity depression and the analogy with Group VIII–Group Ib systems suggest an alternative interpretation, i.e., the metal particle is stationary and the vacancy moves to the perimeter of and onto the particle. This could give rise to a localized electronic interaction, but the mechanism of deactivation would also have a large geometric factor analogous to the Group VIII–Group Ib interaction. By movement of a vacancy onto the surface of a particle we imply the diffusion of a reduced titanium oxide, e.g., Ti_2O_3, onto the surface of the particle. Our model of the HTR deactivation is consistent with the perimeter calculation of ethane and n-butane hydrogenolysis shown in Fig. 1. It would predict that the kinetics of the interaction (amount of deactivation as a function of time at a fixed reduction temperature) would vary with the square root of time as generally observed for diffusional phenomena (*28*). That this is the case is demonstrated in Fig. 5. It should be noted that the migration of a reduced titanium oxide species onto the particle offers an explanation of how the effect can still exist for large particles (*5e*) (while migration only to the perimeter would not) and why SMSI is, in part, reversible by mere oxidation at room temperature (*29*). The latter could be the result of the reoxidation of the reduced titanium oxide species converting a strong chemical bonding into a physical interaction. In the recent study of the Ir/TiO_2 system, Foger notes that SMSI is more easily reversible with small particles than with large, perhaps because the reformed TiO_2 has a comparatively shorter distance to move off the metal particle to reassociate with the bulk TiO_2.

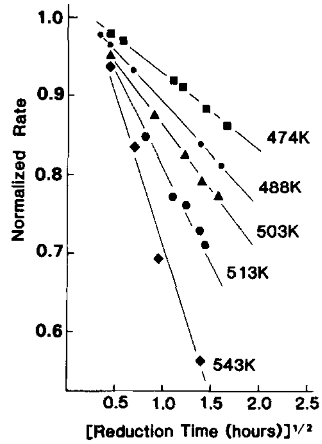

FIG. 5. Evolution of ethane hydrogenolysis activity over Rh/TiO_2 in H_2 atmosphere as a function of square root of reduction time. The rates are normalized to the values extrapolated to time = 0 at each temperature. To perform these measurements, the catalyst, in oxidized form, was placed in a pulse reactor. When the temperature was stable at the desired set point H_2 flow was initiated. Subsequently, the activity was monitored by sending pulses of ethane.

Other workers have suggested the possibility of some titanium oxides species moving onto the metal surface (*8*, *30*). We have provided physical evidence that reduction is necessary but not sufficient (the H atom experiment) and the kinetics of onset of SMSI (Fig. 5) are consistent with a migration step. Moreover, we elaborate on the concept using the analogy with the Group VIII–Group Ib system to suggest that SMSI is the result of a combined geometric (migration of a species from the support) and local electronic interaction (chemical bonding) between the metal and the migrated species.

4. CONCLUSIONS

We conclude that after HTR the Rh particles interact with reduced TiO_2 at the perimeter of the particles and that the interaction energy is sufficient to cause some migration of reduced support species onto the particle. This interaction is strongly deactivating for hydrogenolysis. Because those sites that remain active have an unchanged activation energy and the effect is very analogous to the Group Ib interaction with Group VIII metals, we propose that the deactivation of hydrogenolysis sites is, in part, geometric and that the electronic interaction is localized (essentially chemical bonding). The smallest particles in the distribution are more affected both because of their higher perimeter to surface ratio and because the distance a migrating species would have to move to reach the center of the particle is shorter.

By way of contrast, after LTR there exists a delocalized transfer of charge from the Rh particle to the support. The effect is more evident in the small particles because the screening of the free electrons of the outer metal layers, in large particles, dilute the charge perturbation over one or two atomic distances.

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