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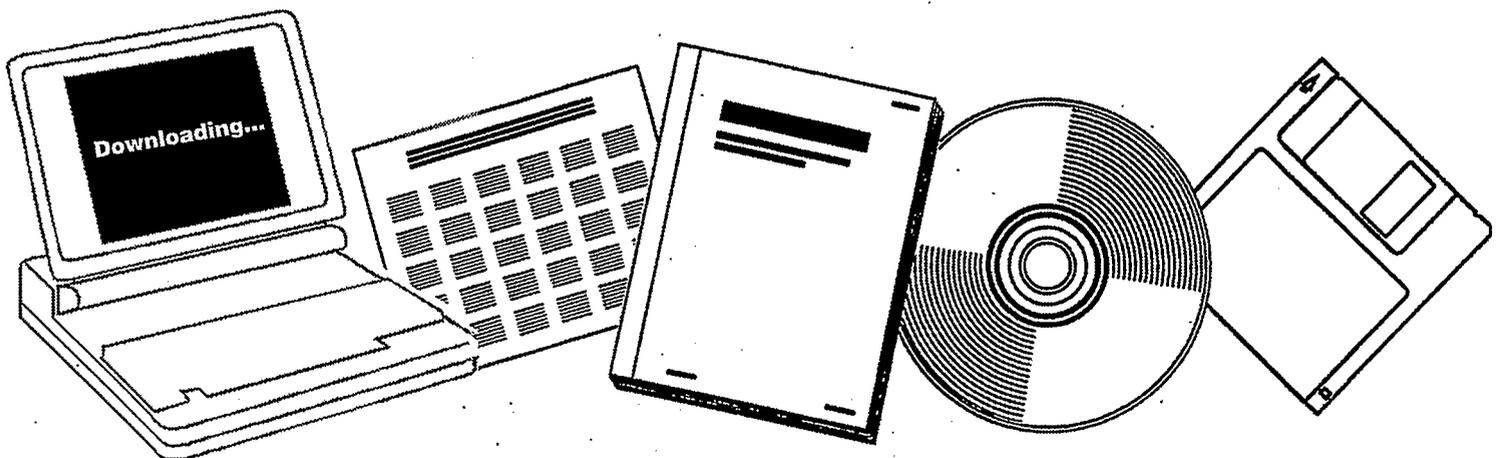
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**GEOMETRIC AND ELECTRONIC EFFECTS OF SMSI
(STRONG METAL-SUPPORT INTERACTIONS) IN
GROUP VIII-TIO SUB 2 SYSTEMS**

YALE UNIV.
NEW HAVEN, CT

1984



U.S. Department of Commerce
National Technical Information Service

CONF-840748--2

DE88 005023

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Geometric and Electronic Effects of SMSI in Group VIII-TiO₂ Systems

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Summary

To date most experiments designed to probe Strong Metal-Support Interactions (SMSI) have focused on electron transfer between the metal and the support. For certain structure sensitive reactions, e.g., hydrogenolysis, SMSI can be understood to be of geometric origin and caused by migration of a species from the support onto the metal particle. We present three kinds of evidence for this model for the Rh/TiO₂ system: Auger sputter profiling of model catalysts, extended X-ray absorption fine structure (EXAFS) analysis and infrared spectra of chemisorbed CO. The hydrogenation of CO and decomposition of NH₃ are, like hydrogenolysis, structure sensitive. However, SMSI has very little effect on these reactions. In the case of CO hydrogenation, SMSI is reversed by the reaction products CO₂ and H₂O. Apparently the most abundant surface species in NH₃ decomposition, chemisorbed N atoms, competes with migrated support species.

Introduction

In the last five years there has been rapid growth in the number of laboratories involved in the study of metal-support interactions. Much of the credit for awakening interest in an old area of catalytic research must be given to Tauster and coworkers at Exxon (1). What makes their contributions more significant than the legion of other papers that report "an effect" of support, additive, etc., on activity or chemisorption is the observation that the interaction between group VIII metals and TiO₂, referred to as a strong metal-support interaction (SMSI), can be induced by a simple chemical treatment of the catalyst (reduction in H₂ at high temperature) and that it can be reversed simply by oxidation and re-reduction in H₂ at low temperature. The reversibility of the metal-support interaction, the unambiguous identification of the interaction with the reducibility of the support and demonstration that TiO₂ is not unique (2) make it unlikely that the effect is an apparent metal-support interaction, i.e., attributable to particle size, support impurity, or other effects (3) which have not been properly controlled. It should be pointed out that Tauster et al. (1) also demonstrated that trivial explanations of the group VIII-TiO₂ interaction such as massive sintering, or complete encapsulation of the metal, may be ruled out experimentally. Moreover, they showed that the extent of interaction could be quantified by the degree to which H₂ or CO chemisorption are depressed.

The most prevalent assumption among research groups studying metal-support interactions has been that the effect is caused by electron transfer. In fact, the electronic properties must always be altered to some degree by the contact potential developed when the metal particle and oxide Fermi levels come into equilibrium at the interface (4). Theoretical (5)

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and experimental work (6-11) suggests, with some exceptions (12), a Group VIII metal-Ti cation bonding accompanied by electron donation from the Ti cation to metal atoms. However, catalytic probes using structure sensitive reactions, e.g., hydrogenolysis, indicate that geometric effects may dominate over electronic effects of metal-support interaction for these reactions (13).

Reduction of Rh/TiO₂ catalysts at 773K causes a large depression in hydrogenolysis activity (about 10⁻⁵ for ethane hydrogenolysis relative to a low temperature reduction), and the magnitude of the effect is the most pronounced for the smallest particles (14). In contrast, cyclohexane dehydrogenation activity is only decreased about a factor of two when activities, after reductions at 473K and 773K, are compared. This behavior is quite analogous to the effect of a group IB metal on the activity of a group VIII metal, e.g., Cu on Ni (15). The similarity between Rh-TiO₂ interaction and group VIII-group IB metals interaction is also evident in the kinetic parameters of ethane hydrogenolysis (13).

The above-mentioned results have produced a working hypothesis that postulates the migration of some species from the support over the metal particle. This migration affects ensemble sites such as an inert group IB metal does. Complete encapsulation cannot result, at least not at 773K, since the rate of cyclohexane dehydrogenation is depressed at most by a factor of two. This does not rule out localized electron transfer between the migrated species and particle as determined by XPS (9), see ref. 13 for discussion.

In this paper we will present direct evidence for migration of a sub-oxide of titanium onto Rh particles obtained from Auger/sputter profile experiments and from extended X-ray absorption fine structure (EXAFS) analysis. The analogy between group VIII-group IB metal-metal interaction and the group VIII-TiO₂ interaction will be strengthened by infrared spectra of CO chemisorption on Rh/TiO₂ as a function of reduction temperature. Some reactions such as CO hydrogenation or NH₃ decomposition, which are usually considered structure sensitive reactions, do not reflect SMSI if one uses the original definition of Tauster et al. (1), i.e., a reversible effect of high temperature reduction. We will present results for these reactions and suggest that, unlike hydrogenolysis, the effects of support on these reactions are only apparent when Rh/TiO₂ is compared to Rh on irreducible supports and that they are manifestations of electronic as well as geometric effects.

Experimental

Ultraviolet photoelectron (UPS) spectra were taken with a double-pass cylindrical mirror electron spectrometer. Carbon monoxide chemisorption was monitored by changes in the UPS spectra, primarily by the appearance of the σ -molecular orbital. The preparation and characterization of Rh films on TiO₂ (110) used for the CO adsorption experiments have been previously reported (16). The EXAFS spectra were obtained in a cell designed for in situ oxidation and reduction. The catalysts used for the EXAFS analysis were those used in a previous study (17). Detailed description of the experimental procedure and analysis will

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be published elsewhere (18). The infrared spectra were obtained by transmission Fourier transform spectroscopy using a conventional heatable, evacuable cell. A complete description of catalyst preparation and the reaction studies can be found in ref. 19.

Results and Discussion

1. Model Catalysts

Model catalysts were prepared by evaporating 1.5 to 4 monolayers equivalent of Rh onto clean TiO_2 (110) (16). Depth composition profiles of these films were obtained using Auger spectroscopy and Ar-ion sputtering. An unreduced catalyst exhibits a monotonically decreasing Rh signal and increasing Ti and O signals with sputtering time, but a sample reduced at 673K exhibits a maximum in the Rh and minima in Ti and O signals as the sample is sputtered (16). These results suggest that a TiO_x species has migrated onto the Rh particles. The fact that the overlayer is a sub-oxide is deduced from the lower Ti/O ratio for the overlayer than for the clean TiO_2 crystal. As observed for powder catalysts, after high temperature reduction, the reduced model catalyst no longer chemisorbs CO. However, sputtering of the reduced catalyst until the Rh Auger signal was near its maximum restored CO chemisorption. This is demonstrated in Figure 1, which shows the UPS spectra for CO exposure of a) polycrystalline Rh and b) a model Rh/ TiO_2 catalyst reduced at 673K in 10^{-3} torr H_2 and then partially sputtered.

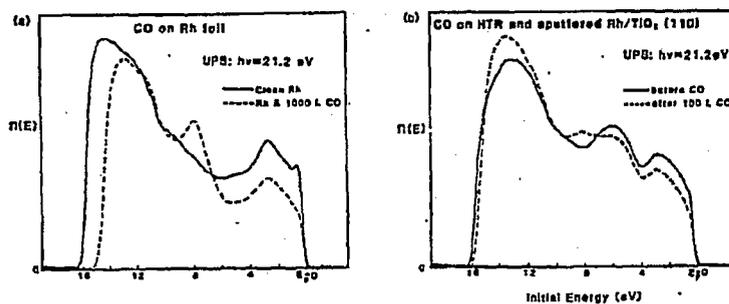


Figure 1: UPS spectra for (a) an atomically clean Rh foil before (solid curve) and after (dashed curve) exposure to 10^3 L CO and (b) for a high temperature reduced and sputtered Rh/ TiO_2 (110) model catalyst before (solid curve) and after (dashed curve) exposure to 100 L CO.

2. EXAFS of Rh-Ag/SiO₂ and Rh-Ag/TiO₂

The original purpose of the EXAFS study was to investigate the effect of support on the Rh-Ag interaction. However, Rh/TiO₂ showed similar behavior (with respect to Rh-O bond formation) to that of Rh-Ag/TiO₂, but the latter EXAFS spectra were obtained with higher signal-to-noise ratio and allow a direct comparison to another catalyst where the preparation was identical except that the support was SiO₂. Figures 2a and 2b show, respectively,

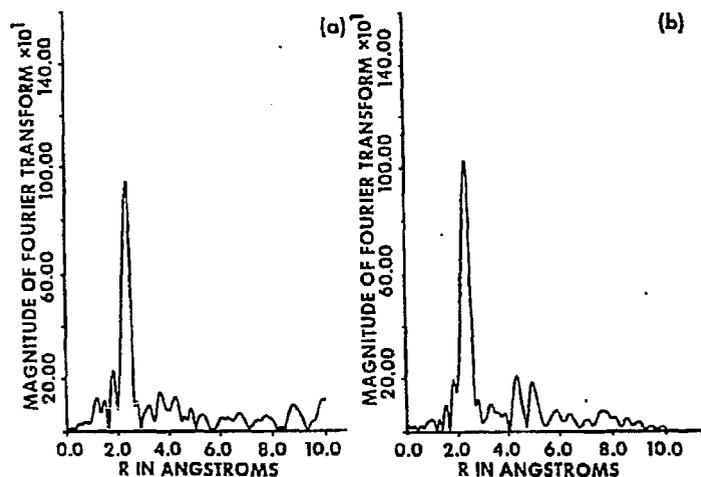


Figure 2: (a) Magnitude of Fourier transform of Rh K edge EXAFS of Rh-Ag/SiO₂ after reduction at 499K for 70 min, (b) after reduction at 753K for 90 min. Spectra recorded at liquid N₂ temperature.

the magnitudes of the Fourier transforms of Rh K edge EXAFS of the low and high temperature reduced Rh-Ag/SiO₂. Comparable spectra for Rh-Ag/TiO₂ are shown in Figure 3a and 3b. The region of interest is below 2 Å in these spectra. A small decrease is observed for the Rh-O peaks when the reduction temperature is varied for the SiO₂ supported catalyst, but on TiO₂ this peak is about 1.5 times as large after a high temperature reduction than after a low temperature reduction. A crude model for the high temperature reduced Rh-Ag/TiO₂ spectrum in Figure 3b is shown in Figure 4a. We have constructed this spectrum by combining the EXAFS of Rh-O neighbors from the Fourier filtered spectrum of RhO₂ and of Rh-Rh neighbors from the Fourier filtered spectrum of Rh foil in a ratio of 1:2, and Fourier transforming these to give the result exhibited in Figure 4a. For comparison, Figure 4b shows the Fourier filtered first Rh-Rh and Rh-O shells of a Rh-Ag/TiO₂ catalyst after high temperature reduction. Curve fitting indicates a Rh-Rh bond length of 2.70 Å and a Rh-O distance of 2.08 Å; coordination numbers for the shells are on the order of 8 and 3, respectively. The qualitative interpretation of these spectra is that there are more Rh-O interactions after

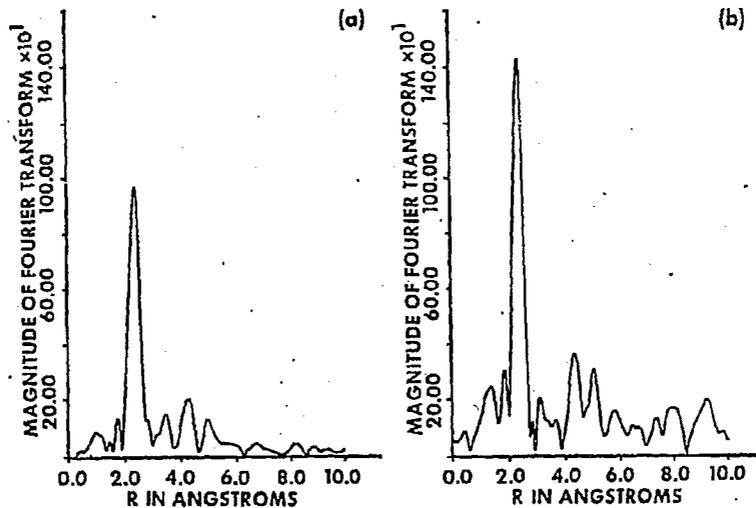


Figure 3: (a) Magnitudes of Fourier transforms of Rh K edge EXAFS of Rh-Ag/TiO₂ after reduction at 487K for 70 min, (b) after reduction at 75% for 90 min. Spectra recorded at liquid N₂ temperature.

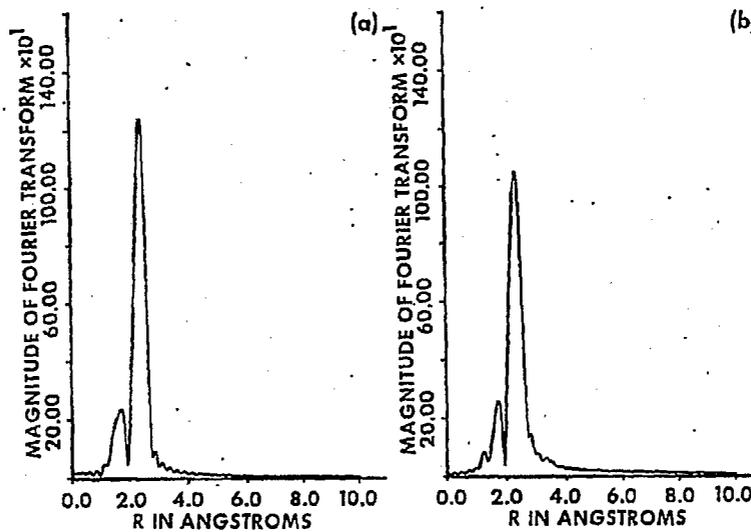


Figure 4: (a) Magnitude of Fourier transform of model EXAFS. The small peak corresponds to oxygen atoms at a mean distance of 1.97 Å from Rh atom. The large peak represents the first shell Rh atoms at 2.69 Å in metallic Rh. (b) Magnitude of Fourier transform of Rh K edge EXAFS of first shells of Rh-Rh and Rh-O in Rh-Ag/TiO₂ catalyst after HTR.

high temperature reduction than after a low temperature reduction. This could be the result of Rh particles spreading out during the high temperature reduction, as previously reported for Pt/TiO₂ (20). In the light of the sputter profiles, however, we take the EXAFS results as additional evidence for Ti sub-oxide migration over Rh particles. These results are in contrast with those recently reported by Short et al. (21) for Pt/TiO₂ where no evidence was found for Pt-O coordination greater than 1/2 atom/Pt for either low- or high-temperature reduction. However, it should be noted that their "high" temperature reduction was 75K lower than that used here, i.e., 673K rather than 748K and, of course, a different metal is involved.

3. Infrared of CO on Rh/TiO₂

In order to probe the surface structure of alloys, Eischens (22) utilized the property of CO to adsorb on a single group VIII atom in a linear fashion, on a pair of such atoms in a bridging fashion and only very weakly or not at all on the group IB metals. He showed that CO, which is predominantly in the bridge structure on Pd and the linear structure on Pt, exhibits a spectrum identical to that of Pt when adsorbed on the equimolar alloy. Eischens concluded that the alloy surface does not have the properties of a simple mixture of the two components and suggested that the absence of bridged CO could merely indicate that there are few adjacent pairs of Pd atoms and that CO does not bridge between a Pd and Pt pair. This view has been confirmed in the more recent work of Somo-Noto and Sachtler on Pd-Ag (23) and Ni-Cu (24) alloys. In both cases, the linear band of CO on the group VIII metal first grows while the bridged band decreases as the alloy becomes richer (in the bulk and on the surface) in the group IB metal; all CO adsorption disappears as the surface becomes completely covered with the IB metal. Parallel behavior is observed for Rh/TiO₂ as it is reduced at ever higher temperatures. Figure 5 shows infrared spectra of the catalyst

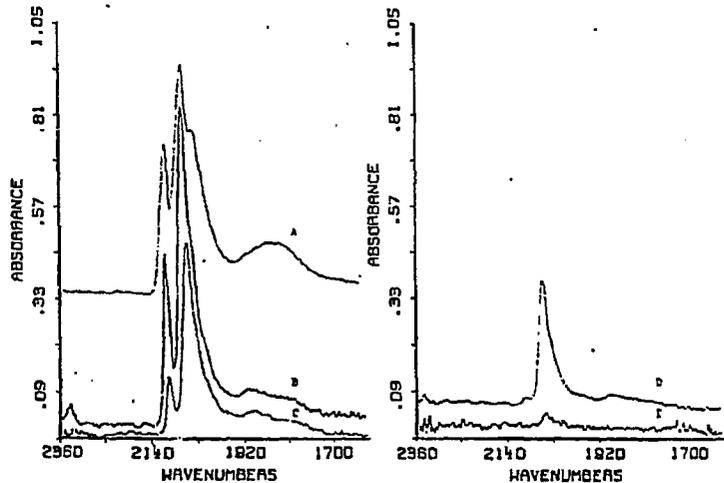


Figure 5: Infrared absorption spectra of CO after saturation and evacuation at room temperature following reduction at: A, 473K for 1 h; B, 517K for 2 h; C, 623K for 2 h; D, 773K for 1 h; and E, 773K for 3 h.

saturated with CO and evacuated at room temperature after several different reduction temperatures. The catalyst was reduced at 473K for one hour and exhibits a bridged band in the region of 1850 cm^{-1} , the linear band 2060 cm^{-1} and a gem dicarbonyl, probably $\text{Rh}^{\text{I}}(\text{CO})_2$, at 2030 and 2100 cm^{-1} (figure 5a). After a two hour reduction the bridged band had mostly disappeared, the linear band had about doubled in intensity and the gem dicarbonyl was not much affected. As the the reduction temperature and time are increased (Figure 5, spectrum C through spectrum B) both the linear and gem dicarbonyl monotonically disappear. Again, we interpret these results as the progressive covering of Rh particles by a species of titanium oxide.

4. CO Hydrogenation

We have studied CO hydrogenation over a Rh/TiO_2 catalyst series of varying dispersion in a steady state flow reactor operating at 1 atm total pressure, 473K, and a H_2/CO ratio of 3:1. To compare the effect of different supports, a Rh/SiO_2 catalyst was also used. Table 1 summarizes CO hydrogenation rates after LTR (low temperature reduction, 473K) and HTR (high temperature reduction, 773K).

TABLE I
CO Hydrogenation Activity

CATALYST	H/Rh	REDUCTION	PRODUCT FORMATION RATE*		
			methane	C2+	alcohols
Rh/SiO_2	0.85	HTR	2.00	0.00	0.01
Rh/TiO_2	0.45	LTR	40.0	1.1	2.4
		HTR	35.0	1.0	2.1
Rh/TiO_2	0.65	LTR	25.0	1.5	1.5
		HTR	23.0	1.1	1.5
Rh/TiO_2	0.76	LTR	30.0	2.1	1.8
		HTR	20.0	2.0	1.3

*Molecules per surface Rh (based on H/Rh) per sec at 473K.

The large variation in rates from SiO_2 to TiO_2 supported Rh indicates a strong influence of the nature of the support on CO hydrogenation. It is interesting to note that even though there are large differences in activity and selectivity when the support is varied, there exists almost no change between the low temperature reduced Rh/TiO_2 catalyst (in a non-SHSI state) and the high temperature reduced catalyst (in the SHSI state). We want to emphasize this fact, which has not received much attention from workers investigating SHSI catalysts. Carbon monoxide hydrogenation has been considered a sensitive probe of SHSI, and it has even been proposed to be ranked first in a hierarchy of testing reactions to decide whether a catalyst exhibits SHSI (25). Morris, Moyes and Wells (26) have critically reviewed some of the work reported on CO hydrogenation over TiO_2 supported catalysts and have pointed out the flaw we are highlighting here. They observe that similar selectivities have been observed after HTR and LTR on Rh/TiO_2 (27) and Pd/TiO_2 (28), indicating that SHSI has no influence on

CO hydrogenation reactions. They also note that many authors, who ascribe the enhanced selectivity to SMSI (29), have not carried out the reaction after LTR to decide whether the observed effects are directly related to SMSI. The misconception probably comes from the fact that most of this work has been done on Ni/TiO₂ catalysts, which require temperatures around 723K to achieve complete reduction of Ni. At those temperatures SMSI is already operative. Indeed, as Morris et al. (26) indicate, the CO hydrogenation reaction itself removes the SMSI. Both oxygen (from dissociated CO) and water (formed during the reaction) are able to restore the normal properties of the metal. Therefore, it is not surprising that SMSI cannot influence CO hydrogenation.

There exists, of course, a support effect evidenced by the variations observed in activities and selectivities when different supports are used. This must not be confused with the SMSI effect, which is the alteration of the normal catalytic properties after HTR caused a modification of the support properties. The support effect observed in this reaction may be related to intrinsic properties of the supporting oxide. For example, Ichikawa (30), studying supported rhodium carbonyl clusters, observed that ZrO₂ and TiO₂ supports improve the selectivity for ethanol formation in the reaction CO-H₂ compared to silica supported rhodium clusters. Katzer et al. (27) have proposed a correlation between selectivity to alcohol formation with the basicity of the support. They found, in agreement with such a correlation, that TiO₂ supported Rh has a much higher selectivity to alcohol formation than the SiO₂ supported catalyst. However, it has been shown (31) that by varying the type of SiO₂ support the alcohol production rate can be greatly altered, and it has been suggested that this enhancement arises from alkaline impurities in some types of SiO₂ supports. Thus, the correlation with basicity may not fully explain the observed trends. In any case, this view emphasizes that enhancement in activity and selectivity for CO hydrogenation reactions must be related to some intrinsic properties of the support, not to the extrinsic SMSI effect.

The strong similarity between group VIII-group IB metal-metal and group VIII-TiO₂ metal-oxide interactions found for some reactions is not observed for the methanation of CO. For example, this reaction is strongly retarded when Cu is added to Ni catalysts (32), while little effect is observed when a Rh/TiO₂ catalyst reduced at high temperature is compared to that reduced at low temperatures. This opposite behavior, rather than weakening our analogy, reinforces the idea that the SMSI is reversed by the CO-H₂ reaction itself. Atomic oxygen and water, formed during the reaction, destroy the interaction. In the case of Ni-Cu catalysts, the activity drops by more than an order of magnitude by adding 10X Cu, while the activation energy remains unchanged. This has been explained by the geometric argument that Cu blocks a part of the ensemble of Ni atoms required to dissociate CO (32). That ensemble, in the case of CO methanation over Rh/TiO₂ catalysts, is kept clean of foreign species by the reaction products themselves. However, it is deactivated for the case of ethane hydrogenolysis, in which the reaction does not significantly affect the interaction.

5. NH₃ Decomposition

We have carried out this reaction over Rh catalysts on three different supports (SiO₂, Al₂O₃ and TiO₂) after LTR and HTR using both a steady state flow reactor and a pulse reactor to search for differences in activity induced by the support or SMSI. Because this reaction is structure sensitive, we might expect, by analogy with other structure sensitive reactions, a large effect of SMSI. In addition, as discussed in Ref. 13, enhanced nitrogen chemisorption on Rh relative to low temperature reduction was obtained after Rh/TiO₂ was reduced at 773K. However, the Rh/TiO₂ catalyst exhibited no significant changes in activity after HTR relative to that observed after LTR (19). Moreover, no effect of the support was observed among the three different supports studied. Almost the same turnover frequencies and similar activation energies were observed in the temperature range studied for the three different supports.

TABLE 2
Ammonia Decomposition on Rhodium Catalysts

CATALYST	TURNOVER FREQUENCY (sec ⁻¹)*		ACTIVATION ENERGY kcal/mol
	at T = 673K, P = 760 torr		
Rh/TiO ₂	(LTR)	0.26	18.0
	(HTR)	0.20	17.0
Rh/SiO ₂		0.34	21.0
Rh/Al ₂ O ₃		0.35	18.0

*Based on N/Rh after LTR.

Table 2 compares turnover frequencies (at 673K, 760 torr of pure NH₃) and activation energies for NH₃ decomposition over the three different catalysts. The SMSI does not appear to affect this reaction greatly. Almost the same reaction rates and activation energies were obtained following LTR and HTR. In agreement with our results, Dumesic and co-workers (34) have found that, for the reverse reaction (NH₃ synthesis), following reduction at 773K, Fe/TiO₂ catalysts exhibit the same activation energy and nearly equal turnover frequency as they do following sequential oxidation at room temperature and reduction at 713K.

Conclusions

The analogy between metal-metal interaction of group VIII-group Ib bimetallic catalysts and the metal-oxide interaction of group VIII-TiO₂ is strengthened by the effect of reduction temperature on CO chemisorption (see Figure 5). Direct evidence for the migration of a sub-oxide of TiO₂ onto Rh particles is obtained from sputter profiling, and it has been demonstrated that this sub-oxide inhibits CO chemisorption. We conclude that SMSI depresses the activity of Rh for hydrogenolysis for the same reason that an inert group IB metal does, i.e., it breaks up or renders inactive the large group VIII metal ensembles which constitute the active sites for this reaction. The hydrogenation of CO and the decomposition of NH₃

are also generally considered to be structure sensitive reactions but are not affected by SMSI (defined as a reversible effect on chemisorption capacity or catalytic activity induced by a high temperature reduction). It is probable that SMSI, the strong binding of a sub-oxide of TiO₂ to the metal surface, is reversed by competitive chemisorption of the products of CO hydrogenation (chemisorbed oxygen and H₂O) and the reactant of NH₃ decomposition (chemisorbed N₂).

Acknowledgements

This work was partially supported by the Department of Energy, Office of Basic Energy Sciences, under contracts DE-AC02-81ER10829 and DE-AC02-81ER10830. Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to the Cornell High Energy Synchrotron Source, where the EXAFS data were obtained.

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