

SMSI in Rh/TiO₂ Model Catalysts: Evidence for Oxide Migration¹

I. INTRODUCTION

Although metal catalysts supported on reducible transition-metal-oxide powders have been the subject of intense study during the last few years, a great many questions remain about the origin of the strong metal-support interactions (SMSI) that occur in those systems (1). In order to remove some of the complications inherent in work on powder catalysts, we have been studying SMSI on model catalysts prepared by depositing various amounts of catalyst metal onto well characterized, single-crystal oxide supports. This note reports initial results on Rh/TiO₂, which indicate that high-temperature reduction (HTR) to the SMSI state is accompanied by the transport of a suboxide of Ti over the Rh particles and that this transport is at least partially responsible for the suppression of CO chemisorption on Rh/TiO₂ catalysts in the SMSI state.

II. EXPERIMENTAL METHODS

The surface geometric and electronic structure of single-crystal TiO₂ has been studied extensively both by our group and others (Refs. (2, 3) and references therein; Ref. (4)). It is possible to prepare surfaces having known densities of surface Ti³⁺ ions by various combinations of annealing in ultrahigh vacuum (UHV) and ion bombardment. All of the work reported here was performed in a UHV surface analysis system. TiO₂(110) samples were annealed at 673 K for 30 min in UHV to produce nearly perfect surfaces having a low density of

Ti³⁺ cations and yielding good low-energy electron diffraction (LEED) patterns. Such substrates are similar to the TiO₂ powder used for normal supported catalysts after calcining in air or O₂. The substrate was mounted on a resistively heated holder and its temperature was monitored with a thermocouple pressed onto the front face of the sample by a Ta clip.

Rh was deposited onto the single-crystal supports at room temperature in UHV (<1 × 10⁻⁹ Torr) by thermal evaporation from a Rh filament. For these studies Rh thicknesses of 1½ to 4 monolayers equivalent were used, as determined by Auger and X-ray photoelectron spectroscopy (XPS); similar results were obtained for all Rh thicknesses in that range. Since high-resolution transmission electron microscopy (TEM) measurements could not be performed on the model catalysts because of the relatively thick single-crystal substrate, the morphology of the deposited Rh could not be determined directly. However, TEM work by Meriaudeau *et al.* (5) on Rh/TiO₂ catalysts indicated that the Rh is present in the form of small particles that are stable under HTR.

Auger, XPS, and ultraviolet photoelectron (UPS) spectra were measured with a double-pass cylindrical mirror electron spectrometer. Carbon monoxide chemisorption was monitored by changes in the UPS spectra after exposure to 100 Langmuir CO (1 Langmuir = 10⁻⁶ Torr-s). Sputter profiles of the model catalysts were performed by bombardment with 500 eV Ar⁺ ions; the absolute sputtering rate is difficult to determine, but it was in the range of 0.1-1 Å/min, depending upon the material sputtered.

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III. RESULTS

All model catalysts were prepared on nearly perfect $\text{TiO}_2(110)$ substrates. The substrates did not chemisorb CO at room temperature, in agreement with measurements on blank TiO_2 powder supports (6). The composition of the surface region was determined from the peak-to-peak amplitudes (in first-derivative spectra) of the 503-eV O Auger peak, the 302-eV Rh peak and the sum of the 387- and 418-eV Ti peaks; the sum of two Ti peaks was used in order to minimize the effect of changes in Auger lineshape with oxide reduction (7). In order to eliminate the effect of fluctuations in electron multiplier gain, the Auger peaks were normalized to the sum of all four peaks, which was found empirically to be nearly constant as the amount of Rh on the surface was varied. (Since only relative changes in Auger peak amplitudes are considered here, the type of normalization procedure used is unimportant.) The relative amplitudes of the Ti and O Auger peaks for the bare substrate are given in Table 1. (The uncertainty in Auger peak amplitude is $\pm 1\%$. There is no significance to the accidental equality of the Ti and O amplitudes.) The ratio of the Ti and O Auger peaks is also given.

After deposition of about $1\frac{1}{2}$ monolayers equivalent of Rh, the Ti and O peak amplitudes decreased as indicated in Table 1. The Ti/O ratio also decreased, presumably due to the shorter mean-free path of Ti Auger electrons. This unreduced model catalyst did chemisorb CO, as indicated by UPS spectra.

TABLE 1

Normalized Auger Peak Amplitudes (%) for Model Rh/TiO₂ Catalysts

	Rh	Ti	O	Ti/O
Before Rh deposition	—	50	50	1.00
After Rh deposition	40	29	31	0.93
After 673 K reduction	23	40	37	1.08

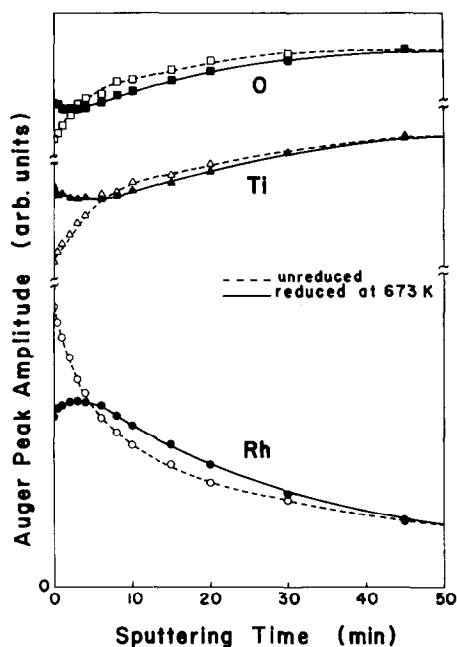


FIG. 1. Auger sputter profiles (Auger peak amplitude versus ion bombardment time) for unreduced (open points, dashed curves) and reduced (solid points and curves) Rh/TiO₂ model catalysts. Curves for Ti and O have been shifted up for clarity.

When an unreduced catalyst was heated to 673 K in either 10^{-3} Torr H₂ or UHV ($\sim 1 \times 10^{-9}$ Torr) for 30 min (HTR), the Rh Auger peak decreased in amplitude and the Ti and O peaks increased, as shown in Table 1. Note that the Ti peaks increase significantly more than does the O peak. This HTR catalyst no longer chemisorbs any measurable amount of CO, in agreement with results obtained on Rh/TiO₂ powder catalysts after HTR (6, 8, 9).

XPS spectra of the Ti 2*p* and Rh 3*d* core levels were taken both before and after HTR. Emission intensity on the low binding energy side of the Ti 2*p* peaks increased after HTR, indicating the presence of reduced Ti species (10). The shape of the Rh 3*d* core levels was unaffected by reduction.

The structure of these model catalysts before and after HTR can be elucidated by sputtering the catalyst metal off of the TiO₂ by means of inert gas ion bombardment. Figure 1 presents the results of such sputter

profiles for both unreduced and HTR catalysts. (The same amount of Rh was deposited on both catalysts.) The unreduced catalyst exhibits the behavior expected for either a uniform film of Rh on TiO_2 or bare Rh particles (dashed curves). The Rh Auger signal falls off monotonically with sputtering time as the catalyst particles are removed, and the Ti and O peaks rise as more support is exposed.

The sputter profile obtained for a model catalyst surface after HTR, shown by the solid curves in Fig. 1, is strikingly different. The Rh Auger peak is initially smaller than for the unreduced sample, as discussed above, but during the first few minutes of sputtering its amplitude *increases*, eventually becoming larger than that for the unreduced sample for the same sputtering times. The Ti and O peaks exhibit the inverse behavior, decreasing in amplitude as the Rh peak rises. For long bombardment times the Rh peak falls and the Ti and O peaks rise, ultimately approaching the same values as those for the unreduced sample.

In order to further elucidate the mechanisms that occur upon HTR, reduced catalysts were sputtered until the Rh Auger signal was near its maximum and then exposed to CO. The reduced, sputtered catalysts *did chemisorb* CO, similar to their behavior before HTR.

IV. DISCUSSION

We have only been able to explain the above results in terms of a model in which a sub-oxide of Ti actually covers the Rh particles after reduction at 673 K (11–16). Sintering and growth of the Rh particles certainly occur during HTR (8), and that is consistent with the reduction in Rh Auger signal and increase in Ti and O signals upon reduction. But that would not give rise to the initial increase in Rh Auger signal with sputtering. The amount of Rh present in both sputter profiles indicates that little if any Rh diffuses into the TiO_2 substrate. The decrease in Ti and O Auger signals that accompanies the increase in Rh signal during

the first few minutes of sputtering can only be accounted for if some Ti oxide physically covering the Rh is removed. The reappearance of CO chemisorption is consistent with this model. Since the Ti/O ratio increases upon HTR to a value greater than that for stoichiometric TiO_2 , we conclude that some reduced Ti oxide must be present. Since annealing the TiO_2 substrate to 673 K does not produce measurable reduction of the surface (Sec. II), we conclude that the sub-oxide resides on the Rh particles.

It is worth noting that the same effects occur in our model catalysts whether they are annealed in H_2 or in UHV. There are two possible interpretations of that result. One is that H_2 is not necessary for the formation and migration of Ti oxides onto the Rh particles and thus that UHV is a sufficiently “reducing” environment for the process. [UHV is a reducing environment for the creation of O vacancies in the bulk of TiO_2 (2).] The other possibility is that H is necessary but that there are enough interstitial H atoms present in the TiO_2 support to drive the process even in the absence of an H_2 ambient. Electron- and photon-stimulated desorption have shown that H is present in the subsurface region of TiO_2 and many other materials (17), although the amounts have not been quantified. Further work is necessary to clarify this point.

Further experiments are underway to study the effects of reoxidation and low-temperature reduction on these model Rh/ TiO_2 catalysts. But the observations reported here offer strong evidence that the SMSI behavior seen in Rh/ TiO_2 catalysts is at least partially due to a physical covering of the catalyst particles by reduced Ti oxide species (11–16).

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