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The Effect of Niobia on the Methanation Activity of a Pt Foil[1]

Recent work examining the interaction between titania and transition metals has indicated that a partially reduced titania overlayer can form on the surface of a titania-supported catalyst (*1–18*). For example, Ko and Gorte have shown that a partial oxide of titania diffuses into a Pt foil at high temperatures and segregates back to the surface at low temperatures (*1*). This can explain how a titania layer could appear at the surface of a supported metal. In addition, we have shown that a Pt foil with a titania overlayer exhibits the same methanation rates as are reported for actual titania-supported Pt catalysts (*2*), even though complete suppression of CO and H_2 adsorption is observed.

Unusual support effects are observed for metals on niobia as well. As with titania-supported catalysts, catalysts supported on niobia can exhibit suppressed adsorption of CO and H_2 while maintaining a high methanation activity (*19–21*). Ko and Gorte have shown that an oxide of niobium also diffuses into Pt at high temperatures and segregates to the surface at low temperatures (*3*). The maximum amount of niobia which could segregate to the surface had a coverage of 10^{15} oxygen atoms/cm^2. This coverage *completely* suppressed CO adsorption at 295 K and H_2 adsorption at 80 K.

To determine whether an overlayer of niobia was responsible for the properties observed with niobia-supported catalysts, we have examined the methanation activity for a Pt foil with a niobia overlayer. Our experimental apparatus consists of a sample attached to a magnetically manipulated, linear-motion feedthrough which can be isolated from an ultrahigh vacuum system. This system allows us to measure reaction rates at atmospheric pressures on a sample which can be characterized by Auger electron spectroscopy (AES) both before and after reaction. This system is described in more detail elsewhere (*2*).

The niobia overlayer was deposited on the clean Pt foil by evaporating a Nb wire near the foil in 10^{-7} Torr O_2. The foil was then heated to 700 K in 10^{-7} Torr O_2 for 10 min followed by heating in vacuo to 1300 K for a few seconds. It was important for oxygen to be in the chamber during niobium deposition in order for the niobium to be properly oxidized. If the sample was not properly oxidized, niobia did not return to the surface after heating the sample to 1300 K in vacuo. This final heating step was necessary to remove excess niobia and was sufficient to reduce the Pt to the metallic state. The resulting overlayer of niobia completely prevented chemisorption of CO at 295 K and H_2 at 80 K, as measured by temperature-programmed desorption. It was stable in 100 Torr CO and 400 Torr H_2 at temperatures up to 773 K.

The AES spectrum for the niobia-covered Pt foil is shown in Fig. 1. Peaks at 105, 121, 132, 167, and 197 eV are characteristic of niobium; oxygen is observed at 508 eV. As discussed previously (*3*), we found that the O(508 eV) peak was sensitive to the electron beam and it was necessary to examine this region of the spectrum first to determine an accurate peak height. This electron beam sensitivity is not observed for oxygen chemisorbed on Pt, indicating

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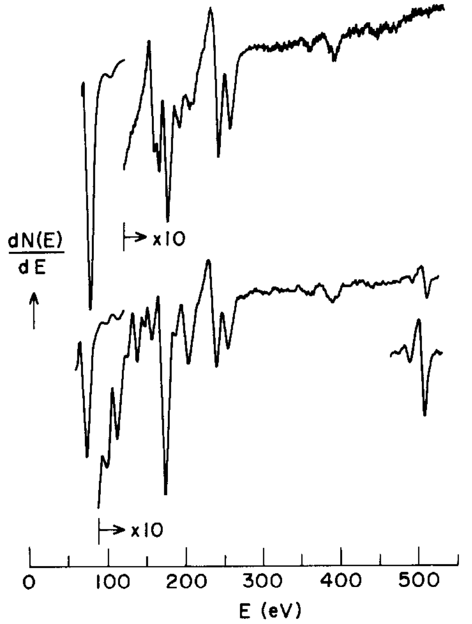

FIG. 1. Auger electron spectra for clean and niobia-covered Pt foils. The O(508 eV) peak was scanned first to determine the peak height before significant electron beam damage had occurred.

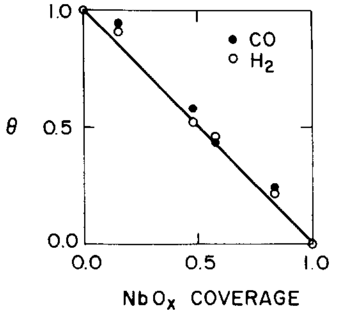

FIG. 2. Saturation coverages of CO and H_2 on a Pt foil, as a function of relative NbO$_x$ coverage as measured by AES. Data were adapted from Ko and Gorte [Ref. (*3*)] by accounting for the small decrease in the Pt(238 eV) AES peak height due to the overlayer when determining NbO$_x$ coverage.

that the oxygen on this surface is associated with the niobia.

Ko and Gorte have shown that the quantities of H_2 and CO that adsorb at 80 and 295 K, respectively, decrease linearly with the Nb(167 eV)/Pt(238 eV) peak ratio (*3*). Correcting the niobia coverage by accounting for the small decrease in the Pt(238 eV) peak height due to the overlayer still gives a linear relationship between the adsorbate coverage and the niobia coverage, as shown in Fig. 2. This shows that the oxide forms an even layer on Pt since three-dimensional clusters would result in nonlinearity. The niobia coverage that *completely* suppressed chemisorption yielded an O(508 eV)/Pt(238 eV) peak ratio of 0.9. Calibrations with known oxygen coverages indicated that this coverage is approximately 10^{15} oxygen atoms/cm^2 (*3, 12*). This coverage is very close to the Pt surface density, showing that the oxide has a very local effect on adsorption.

The methanation rates for 100 Torr CO and 400 Torr H_2 over the niobia-covered Pt foil are shown in Fig. 3. For comparison we have also included the results for clean Pt and for a Pt foil with a titania overlayer (*2*). The dashed lines show the activity of supported Pt catalysts as reported by Vannice and Twu (*21*). The niobia-covered Pt exhibited methanation rates that were essentially identical to those of the titania-covered foil

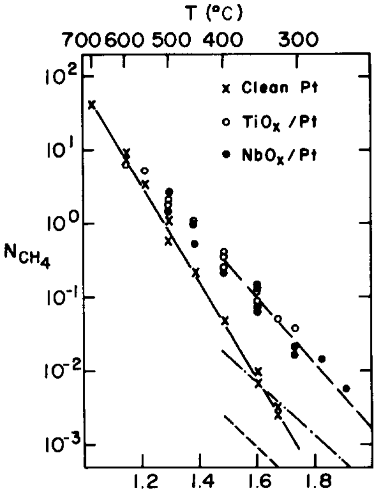

FIG. 3. Methanation rates for 100 Torr CO and 400 Torr H_2 on a Pt foil. The turnover number (N_{CH_4}) is in units of molecules/site second and is based on 1 × 10^{15} sites/cm^2 for the foil. The dashed lines indicate rates reported by Vannice and Twu [Ref. (*19*)] for Pt/TiO$_2$ (————), Pt/Al$_2$O$_3$ (—·—·—), and Pt/SiO$_2$ (– – –). The rates for the niobia- and the titania-covered foils were measured with an oxide coverage sufficient to completely suppress CO and H_2 adsorption.

(*2*) and agreed with those reported for highly dispersed titania-supported Pt after high-temperature reduction (*21*). These rates are significantly different from those observed over the clean Pt foil and alumina- or silica-supported Pt. Over most of the temperature range studied, the activity of the foil was significantly enhanced by the addition of the overlayer of oxide. The activation energy for the reaction over the niobia-covered Pt was 18.7 kcal/mole, the same as that for the Pt with the titania overlayer (*2*). The results shown in Fig. 3 were for a coverage of niobia which completely suppressed H_2 and CO chemisorption. Surfaces with lower niobia coverages exhibited methanation rates between those of the clean and the completely covered surfaces.

The niobia remained on the surface during reaction in 100 Torr CO and 400 Torr H_2 at temperatures up to 773 K. Above this temperature, the surface coverage decreased irreversibly, as measured by AES of the surface following reaction. Apparently, niobia was reduced by the reactant gases at temperatures above 773 K, allowing the niobium to leave the surface irreversibly. We were unable to determine whether the niobium dissolved into the bulk or completely left the sample. A similar reduction and removal of the oxide was observed with titania, except that higher temperatures were needed.

DISCUSSION

The niobia-covered Pt system displays many similarities to titania-covered Pt. These similarities include the dissolution of the oxide at high temperatures and segregation to the surface at low temperatures (*2*), the ability to prevent CO and H_2 adsorption, and the ability to enhance methanation over that observed on the clean surface. This is strong evidence that the support effects observed with both titania and niobia are due to identical causes.

Several explanations for metal–support interactions with titania and niobia have been proposed. One explanation is that electrons are donated from the Fermi level of the semiconducting oxide to the unfilled *d* bands of the metal. The fact that we were able to duplicate the chemisorption and reaction properties of the supported Pt with an oxide-covered surface appears to rule out the need for any such long-range electronic effects. Other studies have led to similar conclusions (*7, 9–11, 13*).

It has also been suggested that the oxide species forms clusters and that enhanced reaction occurs at the interface between the bare metal and the oxide clusters. Our results, however, do not support this model. First, our adsorption results show that the oxide on the metal forms an even layer on the metal and that complete adsorption suppression occurs at an oxide surface density close to that of the Pt surface density. This suggests that there is no cluster-metal interface on our samples. Second, we observed lower reaction rates at lower oxide coverages where there presumably was such an interface. Third, our reaction rates agreed with those observed for normal, titania-supported particles, despite the gross geometric differences between these samples. One should expect to see particle size effects if an interface was important.

Our results indicate that reaction occurs on a surface which has an even layer of oxide above the metal. Results from X-ray photoemission from titania on Pt suggests that a compound of Pt with the oxide is formed at the interface (*13*), a result which is also suggested by the fact that the oxide forms an even layer on the metal. In this compound, presumably, the metal orbitals are still available for interacting with CO and H_2, although the presence of the oxide inhibits the formation of a strongly chemisorbed species.

It should be noted that most reactions are probably not enhanced by the presence of the oxide on the metal surface. For example, the ethane hydrogenolysis activities of Ni/TiO_2 and Ni/Nb_2O_5 are reported to be only 10^{-3} that of Ni/SiO_2 (*19, 22*). This is the normal result one might expect for a surface which is completely covered by an oxide layer. If it were not for the high methanation rates, titania- and niobia-support effects would not be considered unusual. It is probably not possible to determine the reasons for enhanced methanation rates on these surfaces without a more detailed understanding of the mechanism for methanation, which is presently not available.

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