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Characterization of the Interaction between Rhodium and Titanium Oxide by XPS

Recently, a new type of metal–support interaction referred to as a strong metal–support interaction (SM–SI) has been reported for group VIII noble metals on TiO_2 (*1*). The main characteristic of SM–SI is the almost complete suppression of H_2 and CO chemisorption on the supported metal after a high-temperature reduction at 773 K. Oxidation followed by low-temperature reduction at 473 K restores normal H_2 and CO chemisorption activity. Originally, the SM–SI was attributed to a metal–Ti-ion interaction with the metal acting as an electron donor (*1*). Horsley's (*2*) molecular-orbital calculation for SM–SI between Pt and TiO_2 indicates a metal–metal bonding, with the Ti cation acting as a donor to Pt atoms located on surface oxygen-ion vacancies. Effectively, a surface Ti^{3+} ion is converted into a Ti^{4+} ion by electron transfer to a metal atom or cluster. Our X-ray photoelectron spectroscopic (XPS) results for Rh on TiO_2 are in agreement with this model. Fragments of these results have been reported in an abstract (*3*), a grant report (*4*), and two related studies of Rh–TiO_2 interactions (*5, 6*). Here we report representative data for Rh on (0001) TiO_2 and high-area TiO_2 powders by way of comment on the more extensive study of Sexton *et al.* (*7*). We also wish to emphasize that it is only the smallest Rh particles that undergo SM–SI, and that the catalytic properties of these same small particles are affected even when a low-temperature reduction is used, i.e., there exists a Rh–TiO_2 interaction distinct from SM–SI. The low-temperature Rh–TiO_2 interaction increases the rate of ethane hydrogenolysis on small particles relative to large particles or to particles of any size supported on SiO_2 (*6*).

I. MATERIALS AND APPARATUS

The (0001)-oriented single crystals of TiO_2 (rutile) and Al_2O_3 (sapphire) were flame fusion grown from high-purity powder (99.98%) and supplied, cut, and polished by Adolf Miller Company. The crystals were etched in 37% HF for 1 min and ultrasonically cleansed in ethanol and then water before evaporating films of Rh onto the surface in a high-vacuum apparatus external to the spectrometer. Particle sizes were not measured but calibration of infrared internal reflection intensity transmitted by the Al_2O_3 crystals would indicate particle sizes in the range of 25–50 Å (*8*). Two titania powders were used, one provided by Degussa, Inc. (grade p-25, 80% anatase/20% rutile, 50 ± 15 m^2g^{-1}) and one provided by Cabot Corporation (Cab-o-Ti M-85, 85% anatase/15% rutile, 50–70 m^2g^{-1}). The titania was impregnated with a solution of Rh $Cl_3 \cdot 3H_2O$ (Fisher Scientific Co.) or $Rh(NO_3)_3 \cdot 2H_2O$ (Alfa Ventron Corp.), using approximately 4 cm^3g^{-1} of TiO_2 to form catalysts 2% Rh by weight.

XPS of the single crystals was performed in a Yale-built spectrometer (*9*) and also a Hewlett–Packard 5950A. Powders were examined only in the Hewlett–Packard spectrometer. Sample charging was neutralized by an electron flood gun in the Hewlett–Packard spectrometer; the large number of secondary electrons make this less important in the Yale instrument. Reduction was performed in a batch mode at 0.03 kPa hydrogen in the Yale spectrometer. External hydrogen reduction at 10^5 kPa was followed by a second reduction at the same temperature in a steady-state flow of 0.003 kPa of hydrogen in the Hewlett–

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Packard spectrometer. Oxidations were performed at 10^5 kPa outside the spectrometers. Hydrogen adsorption measurements were carried out in a conventional Pyrex volumetric adsorption apparatus by a procedure described in Ref. (*6*).

II. RESULTS

Representative results for both Rh on single crystals and Cab-o-Ti are shown in Table 1. The 2% Rh on Cab-o-Ti catalyst was prepared from $RhCl_3$ impregnation but similar results were obtained when $Rh(NO_3)_3$ solutions or Degussa TiO_2 were used. Because a flood gun was not used for all of the spectra and small shifts in the peak position can be induced by varying the flood gun current, we have reported the difference between the $Rh_{3d5/2}$ peak and $Ti_{2p3/2}$. However, it should be understood that the shift is essentially that of Rh. The $Ti_{2p3/2}$ binding energy referenced to C background at 284 eV is equal to 457.8 eV from which the various Rh binding energies may be calculated. Rhodium films on (0001) Al_2O_3 did not show a difference in binding energy when reductions at 573 and 773 K were compared.

III. DISCUSSION

When the binding energy of initial low-temperature-reduced Rh is compared to the high-temperature-reduced Rh, there is an apparent shift of −0.7 ± 0.1 eV. Subsequent cycling between 773 K reduction, oxidation at 673 K, and 573 K reduction reduces the chemical shift of Rh to an average of −0.2 ± 0.1 eV. A change in the bulk conductivity (and therefore the relaxation shift) of the TiO_2 between the initial and subsequent low-temperature reduction cannot explain the results since this relaxation shift would be expected to affect the Ti^{4+} binding energy as well as Rh and be canceled in $\Delta E = Ti_{2p3/2} - Rh_{3d5/2}$. We believe that the large difference between the initial low-temperature and subsequent low-temperature reduction is due to a sintering of the particles which increases the relaxation shift. Certainly for Pt on TiO_2 there is electron microscopic evidence for sintering (*10*). However, it is also known that the H/M ratio of the initial and subsequent low-temperature reductions can be substantially the same (*1*). Therefore, it is more likely that there is a change in the relaxation shift due to a change in morphology which maintains a high surface-to-volume ratio, e.g., small separated particles change into larger flat (pillbox) particles (*11*).

TABLE 1

ΔE^a of Rh as a Function of Reduction Temperature

LTR[b] (initial)	HTR[c]	LTR[d]	HTR[c]
	Rh on (0001) TiO_2		
	151.7	151.2	151.8
151.0	151.8	151.6	
151.1	151.7	151.6	
151.4	151.8	151.3	
	2% Rh on Cab-o-Ti		
151.0	151.8	151.6	
151.1	151.8	151.9	
	151.5	151.3	151.5

[a] $\Delta E = Ti_{2p3/2} - Rh_{3d5/2}$.
[b] Initial reduction at 573 K.
[c] Reduction at 773 K.
[d] Reduction at 573 K following oxidation at 673 K.

As argued by Sexton *et al.* (*7*), the −0.2-eV difference in the chemical shift of high-temperature-reduced Rh/TiO_2 relative to the second and subsequent low-temperature reductions is a minimum value. That is, to the extent that the pillbox morphology reverts to a three-dimensional particle following oxidation and 573 K reduction a part of the shift to lower binding energy will be compensated by a change in the relaxation shift. Thus, we interpret the −0.2 eV of the SM–SI (high-temperature reduction) as a transfer of negative charge to Rh particles from Ti^{3+} formed by reduction of TiO_2. This same conclusion has been deduced by Chung and co-workers for Pt on (100) $SrTiO_3$ (*12*) and Ni on (110) TiO_2 (*13*). However, it must be emphasized that Ti^{3+} on the surface of the single crystals studied by Chung and co-workers was produced by

Ar-ion bombardment and not by reduction in hydrogen at 773 K. The hydrogen reduction produces a surface concentration of Ti^{3+} which is too small to be detected by photoemission. Because the TiO_2 is obviously reduced by hydrogen at 773 K (it turns blue), we must conclude that *Ti^{3+} is more stable in the bulk than in the surface* and at 773 K the mobility is high enough to remove Ti^{3+} about as fast as it is formed. Evidence for this picture is obtained by angular dependent XPS (*9*) of the (0001) TiO_2 surface. Ion bombardment at room temperature produces Ti^{3+} which is essentially restricted to the surface but the surface concentration can be annealed out by heating (*14*).

Our study of ethane hydrogenolysis over Rh/TiO_2 as a function of dispersion clearly shows that the rate is increased with increased dispersion following a low-temperature reduction (*6*). The rate is dramatically reduced after a reduction at 773 K. By carefully measuring the rate at higher temperature, it can be shown that there is a variation of the rate, the ethane hydrogenolysis rate suffering greater suppression as the dispersion is increased (*15*). This suggests that one might look for an increased XPS shift with increased dispersion, experiments which are now in progress. It also suggests one explanation for the irreproducibility of the results shown in Table 1, where the dispersion was not strictly controlled, although the preparation procedure was always the same. Subsequent hydrogen chemisorption on Rh supported on Cab-o-Sil or Degussa TiO_2 indicates that the dispersions were low (30–40% exposed) for all the samples used to obtain the data in Table 1.

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