Suppression of CO Chemisorption from Aqueous Solution onto Reduced Pt/TiO_2 Catalyst

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The chemisorption of carbon monoxide from a 0.5 M aqueous $KHCO_3$ solution on a prereduced Pt/TiO_2 surface is shown to be completely inhibited as a consequence of a particular chemical state (negative effective charge) of the platinum atoms.

The nature of the interaction between group 8 metals and certain oxide supports, and its influence on the adsorption properties of the corresponding catalysts are the subject of extensive continuing discussion.[1–4] A typical example of this so-called strong metal–support interaction (S.M.S.I.) is given by the platinum/titanium dioxide system which, following reduction at temperatures above 500 °C, exhibits a drastic decrease of carbon monoxide and hydrogen chemisorption.[1] A plausible explanation of such behaviour proposed by Horsley[5] involves distinct charge transfer from Ti^{3+} defect sites in the support to Pt atoms. According to the theoretical calculations,[5] the amount of the resulting effective negative charge on the Pt atom may be as large as 0.6.

Recently, we have reported[6] that reduced Pt deposits on TiO_2 (anatase), obtained by thermal decomposition of an aqueous H_2PtCl_6 solution on titanium-supported 10—20 μm thick TiO_2 films, exhibited a perceptible (up to -0.5 eV) negative shift of binding energy (B.E.) of the Pt core electrons with respect to the values for bulk or supported (but non-reduced) platinum. A remarkable feature of the latter *X*-ray induced photoelectron spectra (X.P.S.) lay in the reversible character of the B.E. shift of the Pt 4f electrons which could be practically annulled and, successively, restored by suitable electrochemical treatment.[6] This strongly suggests that the experimentally observed B.E. shift is actually to be associated with a chemical effect (*i.e.*, the $Ti^{3+} \rightarrow Pt$ charge transfer) rather than with an extra-atomic relaxation effect caused by differences in the particle size. In fact, there is no reason to expect that an ambient-temperature, anodic–cathodic polarization (which, clearly, does not involve platinum oxide formation)[6] could modify the size of the Pt particles.

The present communication deals with the electrochemical behaviour of the above-mentioned Pt/TiO_2 surfaces in solutions saturated with CO. For comparison the investigation was extended to a TiO_2 film electrode which had been platinized in a 10^{-4} M aqueous K_2PtCl_4 solution using a previously described[7,8] photochemical method, instead of the thermal decomposition. X.P.S. analyses of the latter samples confirmed the presence of metallic platinum on the TiO_2 surface, with the Pt 4f B.E. slightly (*ca.* 0.3 eV) higher than in the case of unsupported (bulk) platinum. The preparation conditions were chosen in such a manner that both kinds of electrodes contained comparable amounts of platinum on the surface (10—15 atom % Pt per Ti^{IV}).

As expected, the TiO_2 electrode covered with light-induced (photochemical) platinum deposit, Pt(phot.)/TiO_2, displayed the usual adsorption behaviour of a platinum catalyst towards dissolved CO. This is substantiated by the cyclic voltammogram in Figure 1(a) including two anodic peaks at about 0.1 and 0.8 V *vs.* N.H.E. (normal hydrogen electrode), due to the oxidation of the chemisorbed CO species. A similar cyclic voltammogram, with the two anodic peaks shifted slightly towards more positive potentials, was also obtained for a smooth (bulk) platinum electrode. It should be noted that the detailed form of the voltammograms, the peak ratios and positions, depend to a large extent on the electrode pretreatment and on the sweep rate. The anodic oxidation of CO_{ads}, leading to the formation of CO_2 and/or carbonate ions (depending on the solution pH), usually involves two stages corresponding to the oxidative desorption of two different kinds of chemisorbed species, *e.g.*, weakly and strongly bonded CO_{ads}.[9] The adsorption of carbon monoxide takes place in the 'hydrogen' and 'double layer' potential regions of the platinum electrode and is completed rapidly. In the case of the cyclic voltammogram in Figure 1(a), recorded at a sweep rate of 20 mV s^{-1}, the period of time available for the adsorption was long enough (several seconds) to allow the saturation of the electrode surface with CO_{ads}. In addition, some re-adsorption of CO might take place in parallel with the anodic stripping of CO_{ads} from the Pt(phot.)/TiO_2 surface. The experiments performed with the reduced, thermally formed Pt(therm.)/TiO_2 electrodes did not show any evidence of CO chemisorption despite a long exposure to a CO saturated 0.5 M $KHCO_3$ solution. The corresponding cyclic voltammograms exhibited typically a flat profile in the region of potentials extending between the hydrogen ionization and oxygen evolution regions [Figure 1(b)]. A slight increase of the current, with respect to the voltammograms recorded in the absence of CO, is to be associated with the oxidation of a small amount of products, formed at cathodic potentials, due to the reduction of CO.

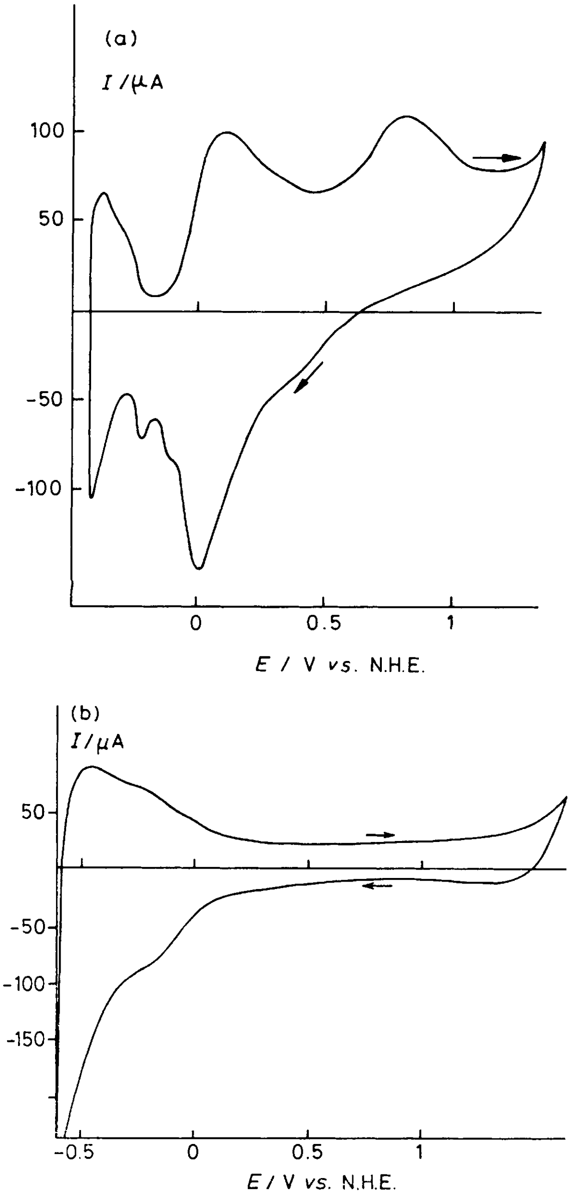

Figure 1. Cyclic voltammetric current–voltage profiles recorded at 20 mV s^{-1} in a 0.5 M aq. $KHCO_3$ solution saturated with CO at 1 atm and 25 °C. Curve (a) corresponds to the anodic stripping of CO_{ads} from the Pt(phot.)/TiO_2 surface and curve (b) shows the lack of CO adsorption on the reduced Pt(therm.)/TiO_2 electrode.

The absence of CO chemisorption together with the lack of platinum oxide formation during anodic polarization of the Pt(therm.)/TiO_2 electrode constitute, to our knowledge, the first example of drastic inhibition of the electrochemical reactions attributable to the interaction between the electrocatalyst and its support. On the other hand, it is interesting that the same Pt(therm.)/TiO_2 electrode has been shown[10] to exhibit significant activity for the cathodic reduction of another carbon oxide, CO_2.

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