Quantum size effects in catalysis by TiO_2/platinum: the switch from partial oxidation to partial hydrogenation of styrene

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Within a restricted range of metal loadings, the presence of small Pt particles on a hydroxylated fully oxidized TiO_2 surface leads to the appearance of unusual chemical behavior. The chemisorption strength of styrene is markedly increased and the partial oxidation activity intrinsic to the hydroxylated titania is replaced by partial hydrogenation activity: styrene is converted to ethylbenzene instead of acetophenone. UPS and X-ray photoelectron spectroscopy data indicate that in this regime of platinum loading the Pt particles are subject to the so-called quantum size effect (QSE) and must therefore be of nanoscopic dimensions. The appearance of hydrogenation activity in the presence of these very small platinum particles may be rationalized in terms of a QSE/bifunctional catalysis mechanism involving water dissociation on the Pt followed by H_a spill-over over at the Pt/titania boundary where captured, strongly bound, styrene molecules undergo hydrogenation.

KEY WORDS: titania; particles; platinum; nanoscopic; quantum size effect; XPS; UPS; styrene; partial hydrogenation; partial oxidation.

1. Introduction

Metal-oxide-supported Pt catalysts are hugely important in chemical technology and have been intensively studied for many years. They are effective for a very wide range of transformations, including hydrogenation, dehydrogenation and oxidation reactions. An emerging recent theme concerns the effect of Pt particle size on the catalytic chemistry where both electronic and geometric effects have been invoked to explain the behavior of very small Pt particles [2,3]. For example, Heiz *et at*. [2] studied CO oxidation over MgO(110)-supported size-selected Pt particles and reported a maximum in the CO_2 production per Pt atom for Pt_{15} particles. They ascribed this optimum activity to energy matching between the Pt HOMO and oxygen LUMO that, it was argued, should facilitate O_2 dissociation. Achatz *et al*. [3] made similar observations when studying methane activation on charged Pt clusters in the gas phase. They found enhanced rates of CH_4 activation on Pt_4^- and Pt_6^+, which they ascribed to the effects of metal particle geometry. These isolated examples of quantum size effects in Pt particles are to be contrasted with the enormous amount of work that has been carried out on many aspects of Pt-catalyzed reactions for which the possible role of such effects has not been explicitly addressed. The present paper is intended as another step in this direction. A significant amount of work has been performed on Pt particles supported on the (110)(1 × 1) surface of single-crystal rutile [4–8], where three-dimensional islands of Pt undergo encapsulation upon thermal treatment [4,5]. No charge transfer occurs between Pt and TiO_2 on stoichiometric rutile whereas, on defective TiO_2, $Ti^{3+} \rightarrow Pt$ local charge transfer is observed [6–9]. Gan *et al*. [10] showed that the (1 × 1) and (1 × 2) TiO_2(110) surfaces behaved differently toward Pt. On the former platinum nucleates randomly, but on the (1 × 2) surface preferential nucleation occurs on the Ti rows, accompanied by $Ti^{3+} \rightarrow Pt$ charge transfer.

Thus far, TiO_2/Pt model studies have focused on single-crystal surfaces loaded with relatively large amounts of platinum: very low loadings that could give rise to quantum size effects [2,3] have not been studied, either spectroscopically or with respect to surface chemistry. Here we report the results of such an investigation in which, moreover, deliberate use was made of a polycrystalline TiO_2 surface so as to mimic more closely the properties of practical Pt/titania catalysts. XPS and UPS were used to study electronic properties of the system, while reactions of adsorbed styrene were used to examine the associated surface chemistry.

2. Experimental methods

Experiments were performed in a VG ADES 400 electron spectrometer system operated at a base pressure of 1×10^{-10} torr. The 10 × 10 × 0.5 mm polycrystalline titanium sample (Advent, 99.6%) was secured to the *xyz* manipulator by spot welding to Ta strips. It could be resistively heated to 1350 K and

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cooled to 100 K. The principal impurities, sulfur, carbon and phosphorus, were removed by sputtering (15 μA/5 keV/900 K) with repeated flashes to 1300 K in order to segregate sulfur from the bulk. XP spectra were obtained with Mg K_α radiation and UPS experiments were performed using a He I photon source. Gas exposure was carried out with a tube doser to enhance the flux at the sample position. Styrene (Aldrich, 99%) and de-ionized water were purified by repeated freeze/pump/thaw cycles and Messer grade 4.8 oxygen was used for the oxidation procedures. Gas purities were monitored by mass spectrometry and quoted exposures are in Langmuirs (1 L = 10^{-6} torr s^{-1}), uncorrected for ion gauge sensitivity. Platinum was deposited using a collimated resistively heated source. Evaporation rates were typically 0.1 ML/min and the background pressure rose to about 5×10^{-10} during evaporation. The deposition rate was calibrated by depositing platinum on titanium metal and comparing intensity ratios of the Ti(2p) and Pt(4f) signals, thus allowing us to quote surface coverages of platinum in equivalent monolayers. Styrene coverages were calibrated by measuring temperature programmed desorption (TPD) spectra as a function of dose, which enabled us to determine the point at which the monolayer was completed and multilayer growth commenced. For TPD/temperature programmed reaction (TPR) measurement (15 K/s) the sample was positioned 2 cm from the collimated quadrupole mass spectrometer (QMS) ionizer so that the signal arose almost entirely from the front face.

The fully oxidized polycrystalline titania surface was prepared by controlled *in situ* oxidation of the clean polycrystalline titanium surface. The oxidation procedure and the characterization of surface composition and morphology by XPS and scanning tunneling microscopy (STM) are described in earlier papers [1,11].

3. Results and discussion

3.1. TPR results: selective hydrogenation of styrene to ethylbenzene by water on Pt/TiO_2

As shown previously [1], hydroxylation of the fully-oxidized TiO_2 surface by exposure to water rendered it active for the *partial oxidation of styrene* to acetophenone. We now show that in the presence of very small Pt particles this same surface also becomes active for the *partial hydrogenation of styrene*. Under the conditions of particular interest here (0.002–0.03 ML Pt, very small metal particles) the acetophenone yield due to the unmodified portion of the sample surface [1] was constant, while the Pt-induced ethylbenzene yield passed through a sharp maximum. At the very highest loading (0.75 ML Pt) both reactions were suppressed.

3.2. Effect of Pt loading on styrene adsorption/desorption

Figures 1–3 show TPR data as a function of Pt loading for desorption of styrene, water and ethylbenzene, respectively, after having adsorbed 0.01 L of styrene on Pt/TiO_2 pre-dosed with 0.03 L water at 130 K. The amounts of styrene (0.01 L) and water (0.03 L) used in these experiments correspond to coverages of 0.02 ML and 0.2 ML respectively. The choice of styrene coverage was determined by the need to avoid swamping the desorption yield measurements by large amounts of unreacted styrene—which indeed occurred at high styrene coverages.

In the absence of Pt, styrene desorbs from fully oxidized polycrystalline titania surfaces at 300 K [1,11]. However, as figure 1 shows, increasing amounts of Pt lead to attenuation of the sharp peak due to desorption from TiO_2 and the appearance of a higher temperature feature (~400–600 K) which shifts to still higher temperatures before being suppressed altogether at the highest platinum loadings. Clearly, the appearance of high-temperature desorption indicates some kind of Pt-induced increase in the strength of styrene adsorption. Note that for Pt loadings of 0.005–0.015 ML (figure 1, traces *c*, *d* and *e*) only high-temperature (400–600 K) desorption of styrene was observed, even though a significant fraction of the surface should have corresponded to unmodified titania sites.

We may understand these results as follows. First note that we have shown previously [12] that styrene is mobile on TiO_2 at 130 K. Thus under TPR conditions at subsaturation coverages of the adsorbate, styrene molecules

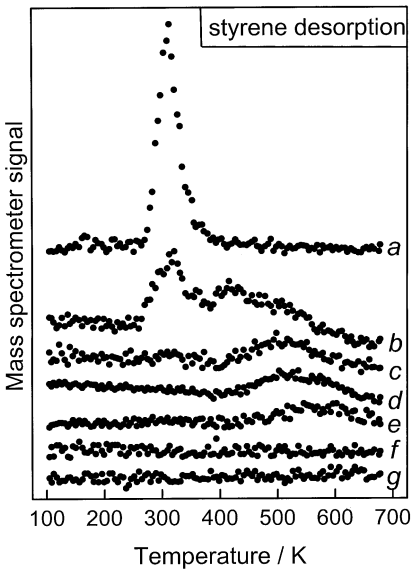

Figure 1. Styrene desorption. Temperature programmed desorption traces for 0.01 L styrene ($m/z = 78$) absorbed on TiO_2 and TiO_2/Pt surfaces following deposition of 0.03 L water at 130 K. Pt loadings (ML): *a* 0, *b* 0.002, *c* 0.005, *d* 0.01, *e* 0.015, *f* 0.03 and *g* 0.75.

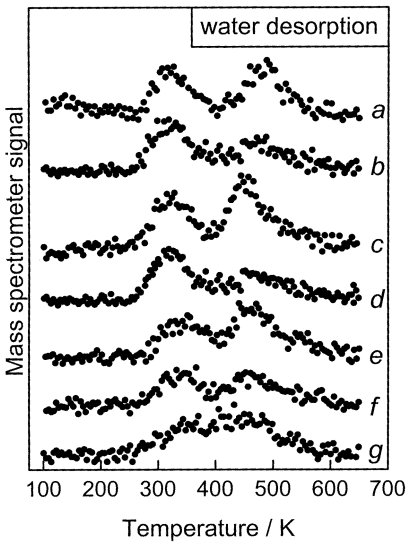

Figure 2. Water desorption. TPR of water from TiO_2 and TiO_2/Pt surfaces following deposition of 0.03 L water and 0.01 L styrene at 130 K. Pt loadings (ML): *a* 0, *b* 0.002, *c* 0.005, *d* 0.01, *e* 0.015, *f* 0.03 and *g* 0.75.

initially adsorbed at unmodified titania can diffuse around the surface. A proportion of these encounter Pt cluster-modified sites where they become more strongly bound, eventually desorbing in the higher temperature peak as the temperature ramp continues. The progressive attenuation and upshift of the high temperature peak suggests that increased adsorption strength is accompanied by increased fragmentation of the molecule. For Pt loadings of 0.03 ML and above (figure 1, traces *f* and *g*) no styrene desorbs below 800 K indicating that when enough Pt is present all the adsorbed styrene cracks at reactive platinum metal sites or platinum-modified titania sites.

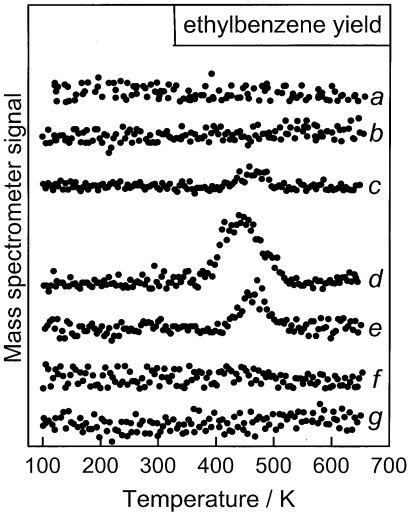

Figure 3. Ethylbenzene yield. TPR of ethylbenzene desorbing from TiO_2 and TiO_2/Pt surfaces following deposition of 0.03 L water and 0.01 L styrene at 130 K. Pt loadings (ML): *a* 0, *b* 0.002, *c* 0.005, *d* 0.01, *e* 0.015, *f* 0.03 and *g* 0.75.

3.3. Effect of Pt loading on H_2O desorption

Figure 2 shows water desorption data acquired simultaneously with the styrene desorption data (figure 1) and discussed above. We have shown [11] that the 340 K and 490 K H_2O peaks from clean fully-oxidized titania correspond to desorption of molecularly-adsorbed water and dissociatively-adsorbed water molecules respectively. It is apparent that the dehydration/dehydroxylation of titania, unlike the desorption of styrene, is not very strongly affected by varying the Pt loading on the surface. The relatively small reduction in water desorption yield over the Pt loading range 0–0.03 ML is consistent with relatively limited blocking of titania sites by Pt. At 0.75 ML Pt loading the two distinct peaks associated with titania sites are replaced by a broad desorption feature centered at ~420 K. This suggests that most of the TiO_2 surface is now either modified or covered by Pt.

3.4. Effect of Pt loading on reaction selectivity

Figure 3 shows the ethylbenzene yields acquired simultaneously with the styrene and water desorption data shown in figures 1 and 2. The ethylbenzene product is unambiguously identified by its characteristic fragmentation pattern $(m/z = 91)/(m/z = 106) = 7/2$ [13], the $m/z = 91$ and $m/z = 106$ spectra mirroring each other with a 7/2 scale factor. It is very evident that (i) addition of Pt to the titania surface switches on partial hydrogenation activity, (ii) this activity appears over only a restricted range of Pt loading and (iii) it passes through a well-defined maximum at ~0.01 ML Pt. No ethylbenzene at all was observed if water had not been previously deposited on the TiO_2. This demonstrates that water is the source of the hydrogen involved in the hydrogenation reaction.

Two possible explanations for the sharp Pt-induced switch in behavior and for its dependence on Pt loading are as follows.

1. TiO_2 undergoes reduction at the peripheries of Pt particles and this TiO_x becomes active for water-mediated hydrogenation [1]. The particle size effect arises because (i) at sufficiently low Pt loadings (<0.01 ML) there is not enough Pt present to reduce a significant fraction of the TiO_2 surface whereas (ii) at sufficiently high Pt loading (>0.015 ML) platinum-induced decomposition of styrene dominates (compare figure 1). Thus it is only at intermediate Pt loadings (0.005–0.015 ML) that the proportions of reduced titania and Pt surface areas are such as to result in detectable hydrogenation activity.
2. A second possible explanation relates to the ability of Pt to dissociatively chemisorb water. Thus although H_2O does not dissociate on extended Pt surfaces [15], quantum size effects arising in very small Pt particles

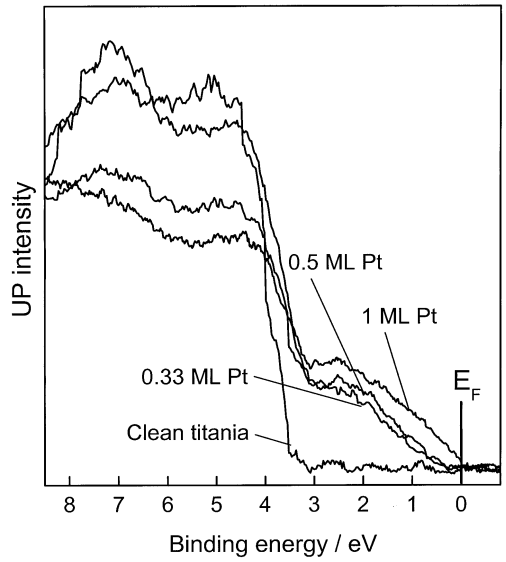

Figure 4. He I UP spectra of TiO_2 and TiO_2/Pt as a function of Pt loading.

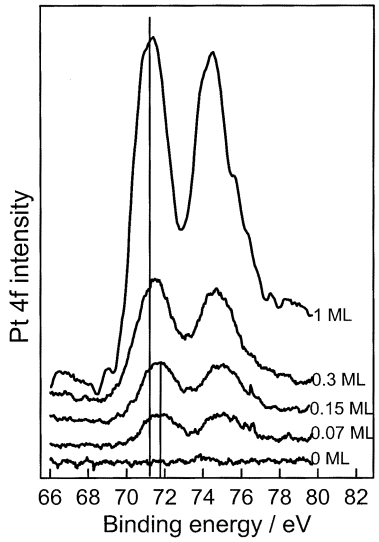

Figure 5. Pt 4f XP spectra as a function of Pt loading.

(0.005–0.15 ML) result in enhanced reactivity and hence water dissociation. Subsequently, H spill-over from the Pt to styrene molecules captured at the metal particle boundary leads to hydrogenation.

The demonstration that such quantum size effects (QSE) do occur in very small Pt particles [2,3] favors the second explanation which corresponds to a QSE/bifunctional catalysis mechanism. Therefore we need to examine whether in the present case there is any evidence for the appearance of unusual electronic properties in our (presumably nanoscopic) Pt particles that are present in the 0.005–0.15 ML range. Photoelectron spectroscopy is capable of providing the information we seek.

3.5. Electronic structure of very small Pt particles

3.5.1. UPS results

Figure 4 shows that addition of <1 ML of Pt on TiO_2 causes the growth of filled states in the band gap but no emission at the Fermi level was apparent until ≥1 ML of platinum had been deposited. This is in line with studies of Pt on single-crystal $TiO_2(110)(1 \times 1)$ [6–8] and indicates that on our titania support the Pt particles involved in the partial hydrogenation of styrene are non-metallic in nature.

3.5.2. XPS results

Figure 5 shows emission from the Pt(4f) levels for a range of Pt coverages on TiO_2. It is clear that at low Pt coverages (<0.3 ML) there is a progressive shift to higher binding energy with the lowest Pt coverage (0.07 ML) giving a total shift of +0.6 eV higher than the value 71.2 eV for bulk Pt [14]. This shift may be attributed to final state effects due to reduced screening of the photo hole in very small Pt particles. It has previously been observed for nanoscopic Pt on fully stoichiometric single crystal $TiO_2(110)(1 \times 1)$ [6,8].

The inference to be drawn from the photoemission data is that in the 0.005–0.15 ML Pt loading range, where unusual catalytic properties arise, we are dealing with nanoscopic Pt particles whose electronic properties are modified by the QSE.

4. Conclusions

1. On fully oxidized, hydroxylated polycrystalline titania, the presence of Pt particles in the range of loadings 0.005–0.15 ML leads to the appearance of unusual reactive properties. The chemisorption strength of styrene is strongly increased and partial hydrogenation activity appears, styrene being converted to ethylbenzene.
2. Photoemission data indicate that these Pt particles exhibit the so-called quantum size effect and must therefore be of nanoscopic dimensions.
3. The appearance of hydrogenation activity in the presence of very small platinum particles may be rationalized in terms of a QSE/bifunctional catalysis mechanism. Water undergoes dissociation on the metal component; the resulting H_a spills over at the Pt/titania boundary where it hydrogenates captured, strongly bound, styrene molecules.

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