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Surface Oxide Films and H_2/CO Chemisorption at the Ru/TiO_2 Interface: Studies with a Model Planar Catalyst

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The properties of high temperature treated (HTT) films of titanium oxide on Ru(0001) have been examined by electron spectroscopy, LEED, and CO/H_2 chemisorption. Starting with as-deposited TiO_x films, surface-to-bulk transport begins at ~700 K provided that the initial oxide loading exceeds 0.68 ML. The system stabilises at ~1400 K with formation of a tenaciously held residual oxide film which is shown by LEED, Auger, and XPS measurements to be an expanded monolayer of TiO. No surface → bulk transport occurs for TiO_x loadings below the critical value of 0.68 ML. Chemisorptive properties have been studied as a function of HTT-TiO_x film coverage and the results are discussed with respect to the SMSI phenomenon.

1. INTRODUCTION

Planar model catalysts prepared by depositing support material on macroscopic metal specimens have been successfully employed to investigate aspects of metal-support interaction (*1–3*), and in the case of the SMSI phenomenon this approach can represent a particularly attractive strategy (*4*). It is well known that a number of different explanations has been advanced to explain SMSI behaviour, including migration of partially reduced oxide support species through or across the metal particles. Such behaviour would obviously strongly affect the availability of chemisorption sites and possibly also modify their reactive behaviour (*5–8*). An alternative type of explanation involves alloy formation between metal and support species (*9–13*) although the nature and constituent elements involved in such alloys are not clear.

In our earlier study of the Ru(0001)/TiO_2 system, we showed how the presence of TiO_2 moieties led to no more than simple site-blocking towards subsequent CO and H_2 chemisorption (*14*). The present paper describes the effect of temperature on this system with specific reference to the formation of TiO_x species that are stable at high temperature, their partitioning between surface and bulk, and the consequences of this behaviour for hydrogen and CO chemisorption. The TiO_x films are produced by high temperature treatment and differ significantly in their surface chemistry from the unannealed TiO_x ($x > 2$) films described in our earlier work (*14*). Use of a single-crystal specimen avoids the problems associated with grain boundary diffusion (*15*) which can dominate the behaviour of polycrystalline samples in experiments of this kind; we therefore have the possibility of determining unambiguously whether TiO_x can be transported into the metal phase at temperatures relevant to SMSI (*16*).

2. EXPERIMENTAL

A description of the apparatus and methods of specimen preparation and cleaning has been published elsewhere (*17*). Deposition of titanium oxide onto the single-crystal

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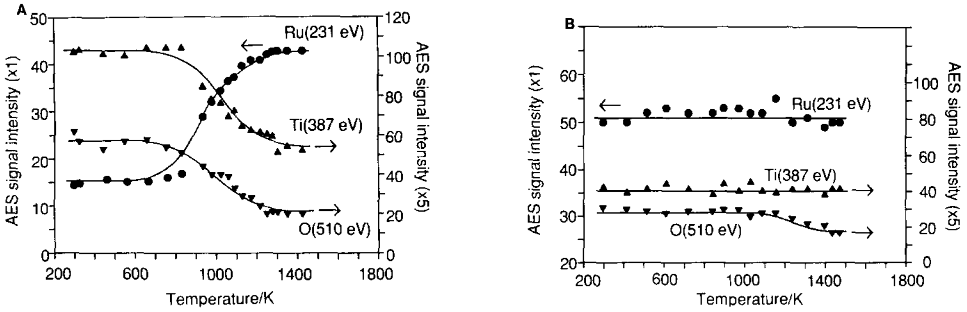

FIG. 1. Variation of AES intensities with temperature for (a) 2.2 ML TiO_x/Ru(0001) and (b) 0.6 ML TiO_x/Ru(0001).

surface was carried out by controlled evaporation of Ti metal from a collimated source operating in an ambient atmosphere of 1×10^{-6} Torr O_2. We have shown previously (*14*) that this procedure results in the formation of an ultrathin layer of TiO_x film whose as-deposited stoichiometry corresponds to $x = 2$ at the point of monolayer completion. Selective removal of oxygen chemisorbed on the exposed Ru metal surface is achieved by holding the specimen at 573 K and irradiating with a flux of hydrogen atoms and ions issuing from a hot cathode low energy source (*14*), a procedure which does not significantly perturb the TiO_x film itself. By this means, patches of TiO_x were generated on an otherwise bare Ru surface. In obtaining the results which follow, each experiment was carried out by rigorously cleaning the surface (*17*), depositing a fresh dose of TiO_x, followed by selective removal of the oxygen chemisorbed on Ru. Quoted TiO_x coverages were obtained by means of a calibration previously established with the aid of LEED/Auger spectroscopy data (*14*); 1.0 monolayer (ML) refers to a monolayer film of as-deposited TiO_x at room temperature.

3. RESULTS

3.1 Temperature-Dependent Behaviour of TiO_x on Ru(0001)

Figure 1A shows the behaviour of an initial 2.2-monolayer film of TiO_x as a function of increasing temperature. The data were obtained by following the Auger electron signal intensities due to Ru (231 eV), Ti (387 eV), and O (510 eV), in each case after heating the sample for a fixed interval of 60 s at various increasing temperatures. In any given case, it was found that quenching the sample to room temperature led to no observable change in signal intensities, so that the data were acquired at room temperature. It can be seen that at sufficiently high heating temperatures (~1350 K) all three signals tend to limiting values. This type of behaviour could be due either to agglomeration of TiO_x at the surface or to diffusion of either Ti or Ti + O into the bulk of the metal.

Once the system had reached its limiting high temperature condition, limited Ar^+ etching of the surface at 300 K resulted in an Auger spectrum corresponding to clean Ru, essentially all Ti and oxygen having been removed. This is illustrated in Fig. 2 which shows a sequence of Auger spectra corresponding to (A) an initially clean surface, (B) after depositing 1.1 ML at room temperature, (C) the result of subsequent heating to 1550 K, and (D) following Ar^+ cleaning at 300 K followed by annealing to 600 K. Further annealing to 1550 K followed by cooling to room temperature led to the appearance of Auger signals characteristic of TiO_x (Fig. 2E). Heating in oxygen (120 L at 1300 K) indicated no further segregation of TiO_x (Fig. 2F). (This procedure is known to leach out dissolved titanium from bulk ruthenium (*17*)). It is noteworthy that, as judged by Auger intensities, the

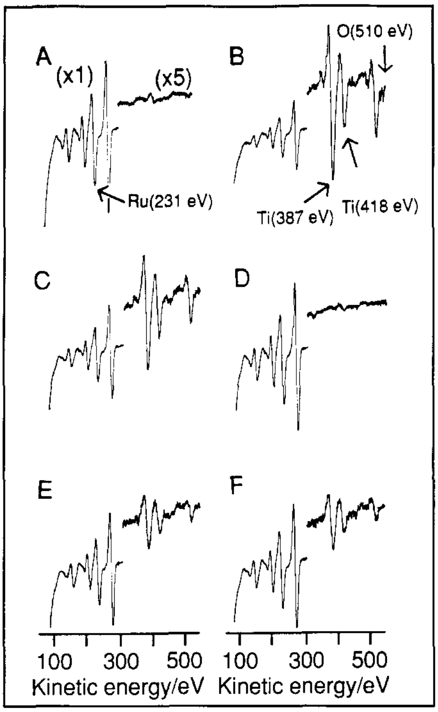

FIG. 2. (A) AES spectrum of clean Ru(0001); (B) after deposition of 1.1 ML TiO_x at 295 K; (C) following a flash to 1550 K; (D) argon ion cleaned and annealed to 600 K; (E) following flash to 1550 K; (F) after heating in 120 L O_2 at 1300 K followed by flashing to 1550 K.

amount of TiO_x initially present (i.e., before annealing) is equal to the amount remaining after annealing plus the amount dissolved (and subsequently re-exposed by etching and segregation).

These data imply that high temperature treatment of TiO_x overlayers on ruthenium result in a limiting coverage of TiO_x (0.68 ± 0.04 ML) which remains on the surface while the remainder diffuses into the bulk. For initial loadings of TiO_x less than this critical amount, no diffusion of TiO_x into the bulk occurs (Fig. 1B). Equally, for initial loadings of greater than 0.68 ML, annealing to ~1500 K results in surface-to-bulk diffusion until a coverage of 0.68 ML remains at the surface (Fig. 3). Figure 4A shows the LEED pattern characteristic of this 0.68-ML TiO_x overlayer. It may be interpreted in terms of a $(5\sqrt{3} \times 5\sqrt{3})R30°$ coincidence lattice formed between the TiO_x overlayer and the Ru(0001) substrate (Fig. 4B). In terms of this model, the calculated fractional coverage TiO_x/Ru is 0.64 ± 0.04, in very good agreement with the overlayer coverage as determined by Auger spectroscopy. XP spectra (Fig. 5) taken from freshly deposited TiO_x overlayers and from the annealed system revealed substantial shifts in titanium core level binding energies (BEs). For the as-deposited TiO_x film the Ti($2p_{3/2}$) BE was 459.2 eV. Annealing of such films to ~1500 K to produce the 0.68-ML TiO_x phase gave a substantially reduced Ti($2p_{3/2}$) BE of 456.0 eV. This 3.2 eV decrease in BE is consistent with the transformation $TiO_2 \rightarrow TiO$ (*18*). Desorption measurements were carried out on multilayer as-deposited films (i.e., unannealed) using a collimated quadrupole mass spectrometer with good detection sensitivity for species desorbing from the front face of the specimen. No signals were detected at mass numbers of 32(O_2), 48(Ti), 64(TiO), or 80(TiO_2); this tends to confirm that the changes in TiO_x coverage which result from heating are due to surface → bulk diffusion and not the evaporation of surface species.

3.2 Carbon Monoxide and Hydrogen Chemisorption

The known TPD fingerprint spectrum for CO from clean Ru(0001) is used to investigate the influence of the reduced titanium oxide species (i.e., after annealing) on

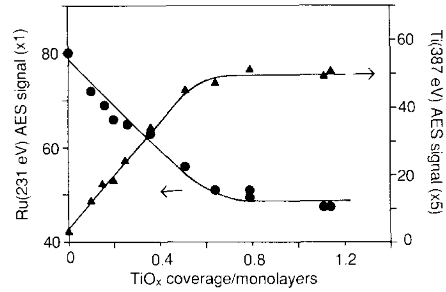

FIG. 3. AES signals after annealing to 1550 K as a function of TiO_x/Ru(0001) precoverage.

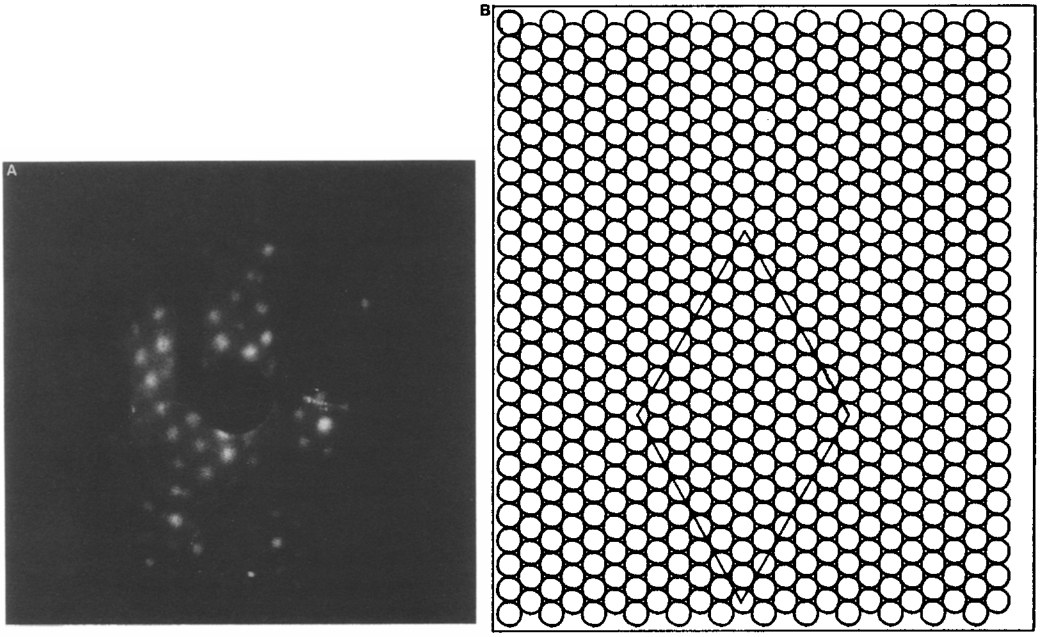

FIG. 4. (A) LEED pattern of $TiO_x/Ru(0001)$; 1.1 ML precoverage flashed to 1550 K (beam energy = 131.7 eV); (B) showing $(5\sqrt{3} \times 5\sqrt{3})R30^\circ$ unit mesh of corresponding coincidence lattice.

neighboring ruthenium sites, and the results are shown in Fig. 6A for a range of TiO_x precoverages. It can be seen that with increasing TiO_x coverage, the CO desorption shifts to higher temperatures. Furthermore, examination of the CO desorption yield as a function of TiO_x coverage (Fig. 6B) shows a non-linear attenuation of CO uptake; this is interesting because the behaviour is markedly different from the simple linear CO site blocking behaviour exhibited by unreduced titanium oxide species (i.e., un-annealed oxide films) (*14*). (In Fig. 6B the uptake at zero TiO_x coverage corresponds to saturation coverage of CO on bare Ru(0001).)

The essentially complete suppression of CO uptake at TiO_x coverages below 1 ML (Fig. 6B) is consistent with expansion of the TiO_x overlayer upon annealing *for room temperature precoverages* < 0.64 *ML* TIO_x. Adsorption/desorption experiments carried out with $^{13}C^{16}O/^{12}C^{18}O$ mixtures showed no evidence for isotopic scrambling indicating that only molecular CO adsorbs and desorbs from the TiO_x-modified Ru surface.

In our earlier work (*14*) we reported that hydrogen chemisorption was drastically inhibited by as-deposited TiO_x (i.e., unannealed films) and that subsequent desorption of H_2 was shifted to lower temperature. In the present case, the decrease in H_2 chemisorption with *annealed* TiO_x precoverage is less marked, taking account of the fact that in this case 0.64 ML of TiO_x precoverage is sufficient to completely block the ruthenium surface (Figs. 7A,7B). Furthermore, in this case, as distinct from the as-deposited case, there is a shift of hydrogen desorption to *higher* temperatures with increasing TiO_x precoverage.

4. DISCUSSION

The present results show that the method and temperature of preparation of TiO_x overlayers on metal surfaces can be critical in determining the metal coverage and chemisorption behaviour of such systems. Such factors may have led to apparent discrepancies resulting in disagreements about the actual role of TiO_x moieties on

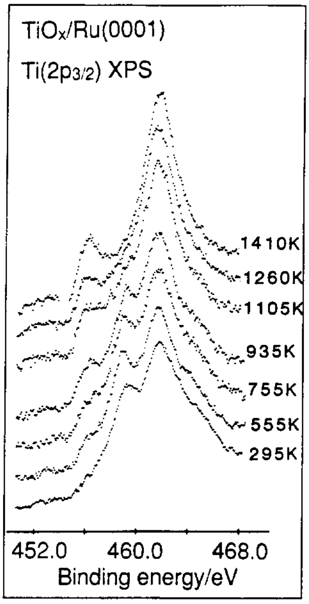

FIG. 5. XP spectra as a function of annealing temperature of a TiO_x film. Note that the large feature around 462 eV is mainly due to the Ru($3p_{3/2}$) level with some contribution from Ti($2p_{1/2}$).

metal particles (*19*). Thus in some cases it has been argued that the effect of such species is simply to block metal sites to chemisorption (*20, 21*), whereas other reports indicate that a longer range effect operates, with adjacent metal sites also being affected by adsorbed TiO_x (*22, 23*).

The formation of a residual tenaciously held TiO_x overlayer after high temperature treatment is somewhat reminiscent of the behaviour exhibited by Ti films on Ru (*24*): however, in the present case, the limiting Ti coverage (0.68 ML) is greater than with the metal-only system (0.49 ML). This presumably reflects the effect of oxygen–Ti binding in stabilising Ti at the metal/gas interface. Not surprisingly perhaps, transport of TiO_x into Ru is also significantly harder than that of Ti alone; diffusion becomes appreciable at ~700 K in the former case and at ~500 K in the latter. It is not possible to comment on whether in the present case the diffusion mechanism involves transport of an intact titanium oxide species as opposed to decomposition

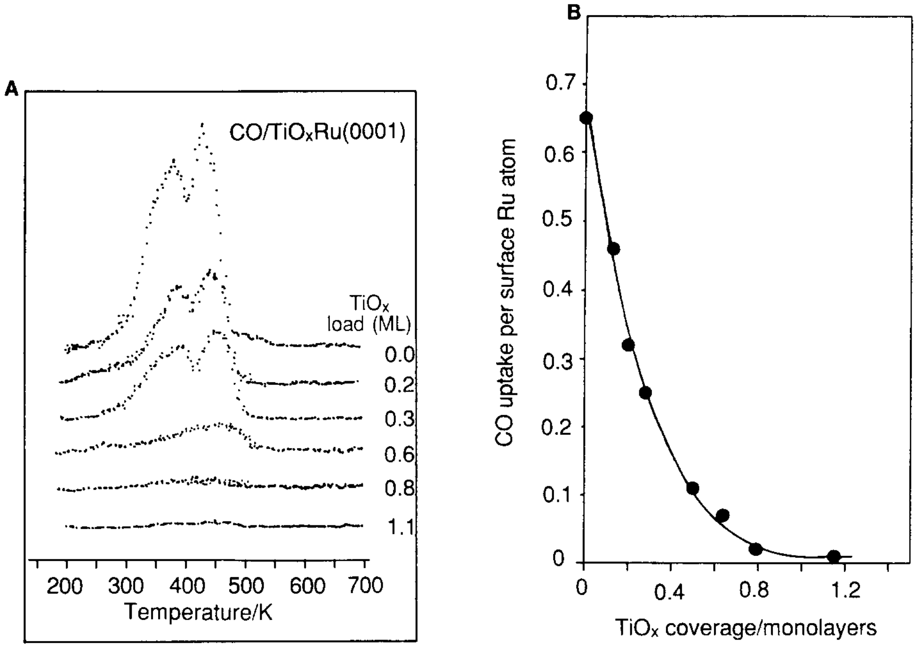

FIG. 6. (A) TPD spectra as a function of TiO_x precoverage following 44-L CO doses at 140 K; (B) molecular CO uptake per surface ruthenium atom.

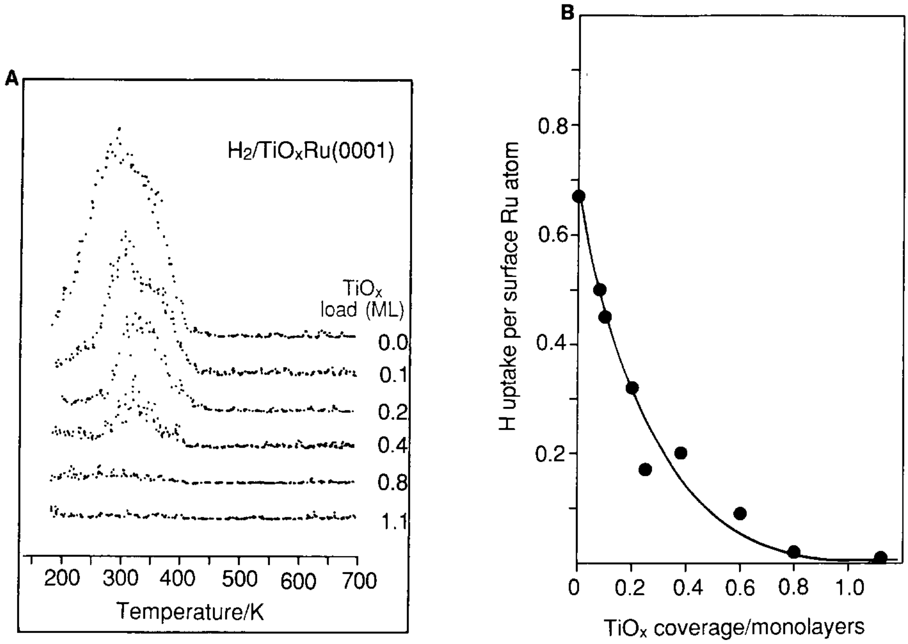

FIG. 7. (A) TPD spectra as a function of TiO_x precoverage following 200-L H_2 doses; (B) amount of H uptake per surface ruthenium atom.

of TiO_x at the surface followed by substitutional diffusion of Ti and interstitial diffusion of the associated oxygen atom. What is clear, however, is that the presence of Ti substantially lowers the activation energy for oxygen diffusion into bulk ruthenium because it is well known that oxygen alone does not diffuse into Ru metal under conditions similar to those implied here (*25*).

Taken together, the Auger, XPS, LEED, and TPD observations are consistent with the view that high temperature treatment of TiO_x/Ru(0001) leads to a reduction in oxidation state of the Ti^{n+} ions. (Our earlier work on as-deposited submonolayers of TiO_x indicated $n > 2$ for such systems (*14*).) The lattice parameter of defective titanium monoxides is proportional to the degree of reduction (*26*) and this is in good agreement with the observed expansion of the TiO_x monolayer film deduced from the Auger and LEED data; the XPS observations confirm a reduction in Ti oxidation state as a result of high temperature treatment.

It seems plausible that the presence of reduced Ti ions in the high temperature treated TiO_x film should lead to some electronic charge transfer to neighbouring Ru atoms resulting in the observed increase in CO chemisorption strength on these atoms. On clean Ru(0001) CO molecules are linearly bonded at on-top sites, and at high coverages interactions in the compressed adsorbate layer are accommodated by a marked tilt of the CO molecules away from surface normal (*27, 28*). The non-linear decrease in CO uptake with increasing coverage of high temperature treated TiO_x may reflect the increased Ru–CO interaction which could inhibit the formation of a compressed CO overlayer.

The corresponding behaviour towards hydrogen chemisorption may be understood as follows. For as-deposited TiO_x films (*14*) highly dispersed titanium oxide species decrease the number of Ru ensembles available for dissociative chemisorption of H_2; high temperature treatment leads to the coalescence of the TiO_x species to produce larger islands (detectable by LEED) leaving a larger number of active ensembles and increasing the hydrogen uptake capacity. An additional possibility is that edges of the HTT-TiO_x islands function as active centres for H_2 dissociation (*29*) followed by spillover onto neighbouring Ru. It is interesting to note that in CO/H_2 competitive chemisorption, any changes which favour the relative amount of H_{ad} could enhance the propagation step in Fischer–Tropsch synthesis, thereby affecting the product distribution (*30–32*), as has indeed been reported for systems exhibiting the SMSI effect (*33*).

5. CONCLUSIONS

The surface properties and chemisorptive behaviour of TiO_x on Ru are strongly dependent on temperature and initial loading. The LEED and Auger data show that high temperature treatment can result in material transport and formation of a new surface phase. In particular, if the oxide loading exceeds a critical value, high temperature treatment results in surface-to-bulk diffusion of both titanium and oxygen leading ultimately to the formation of a stable residual monolayer film of expanded TiO. The XPS results show that reduced titanium species are formed after high temperature treatment. These reduced titanium species at the metal surface transfer electronic charge to Ru; TPD observations reveal associated changes in CO and hydrogen chemisorption behaviour which closely resemble those reported for catalysts in the SMSI condition. It is noteworthy that these phenomena of oxide dissolution and residual TiO surface film formation occur at temperatures similar to those required to induce SMSI behaviour in practical catalysts.

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