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ADSORPTION OF CARBON MONOXIDE ON Ni/Ti AND Ni/TiO_2 SURFACES PREPARED *IN SITU* IN THE ELECTRON SPECTROMETER: A COMBINED UPS-XPS STUDY [+]

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Adsorption of CO on a clean Ti surface is partly associative at 80 K with a $1\pi-4\sigma$ separation of 4.2 eV, becoming dissociative at 130 K. On Ni- covered Ti surfaces, however, associative adsorption ($4\sigma-1\pi$, 3.3 eV) occurs at 80 K and partial dissociation, around 200 K. TiO_2 is reduced more effectively on annealing, when it is covered with Ni. On the surfaces of Ni deposited on TiO_2, there is only dissociative adsorption, unlike on Ni/Al_2O_3 and Ni/TiO_2 (non-annealed) surfaces.

1. Introduction

Modification of the electronic and chemisorptive properties of metallic alloys compared to those of the component metals (the so-called ligand effect) has been considered to be the cause of change in catalytic activity on alloy formation. Studies of the adsorption of CO on alloys such as Pt_3Ti have thrown light on such ligand effects [1-3]. There is also evidence in the literature that on alloy formation, Ni(d) bands get filled by hybridization. We have been examining the interaction of CO with the surfaces of Ni deposited on Al [4] and other metals for some time and we report here the results of our study with Ti surfaces modified by small coverages of Ni. More importantly, we have investigated the surfaces of Ni deposited on oxidized Ti by X-ray and UV photoelectron spectroscopy, as a model system to simulate strong metal-support interaction. As part of this study, we have examined the interaction of CO with such a Ni/TiO_2 surface prepared *in-situ* in the electron spectrometer. We find the adsorption behaviour of CO on Ni-covered Ti surfaces to be similar to that on Ni-Ti alloys [5], being associative around 80 K and dissociative at 200 K and above. It is noteworthy that on a clean Ti surface, adsorption of CO is partly associative at 80 K with a much larger $1\pi-4\sigma$ separation than on the Ni/Ti surface. On the annealed Ni/TiO_2 surface, adsorption of CO is entirely dissociative, unlike on Ni/Al_2O_3 and non-annealed Ni/TiO_2 surfaces.

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2. Experimental

UV and X-ray photoelectron spectroscopic studies were performed with a VG ESCA 3 Mark II spectrometer fitted with a sample preparation chamber (2×10^{-10} torr). A pure polycrystalline Ti foil (Alfa, 99.7%) was spot welded on a sample holder, the temperature of which could be varied from 80 to 800 K. The surface of the foil was cleaned by repeated Ar-ion etching and heating. Ni was evaporated from a tungsten filament on which fine Ni wires (99.9%) were wrapped. AlK_α (1486.6 eV) and HeII (40.8 eV) radiations were employed for the study. Pure CO gas was prepared by the dehydration of formic acid and the purity of the gas checked by means of a mass spectrometer fitted to the preparation chamber. The binding energies are referred to the Ti ($2P_{3/2}$) level of clean Ti at 453.0 eV. Surface concentrations are calculated using a method described by Carley and Roberts [6]. The TiO_2 support was prepared by the interaction of oxygen with the clean Ti foil in the sample preparation chamber. TiO_2 layers of ~ 50 Å thickness were obtained in this manner. Ni was deposited on this oxide surface by evaporation, to the desired coverage.

3. Results and discussion

In fig. 1 we compare the HeII spectra of a Ti surface covered to different extents by Ni with the spectra of clean Ti and Ni surfaces. The spectra clearly indicate that Ni-Ti alloys are formed on the surface when Ni is deposited on Ti. Thus, at a coverage of 1.5×10^{15} atoms/cm^2 (σ Ni), the surface is similar to that of NiTi. The Ni ($2P_{3/2}$) core level spectrum (inset of fig. 1) shows a shift of 0.9 eV to higher binding energy in Ni/Ti compared to clean Ni; there is also a decrease in the Ni (2p) satellite intensity and a larger separation between the main peak and the satellite. The Ti($2P_{3/2}$) level is shifted to higher binding energy by 0.4 eV accompanied by some broadening (inset of fig. 1). Even a small coverage of Ni ($\sigma Ni = 0.5 \times 10^{15}$ atoms/cm^2) gives rise to a distinct Ni(d) band which becomes increasingly prominent with increasing Ni coverage. The Ni(d) band moves away from E_F at small σNi and gets closer to E_F at high σNi. The changes observed by us in the valence band and core levels when Ni is deposited on Ti are similar to those reported in the case of Ni alloys and are likely to arise from the mixing of the Ni and Ti levels [7,8].

Adsorption of CO on a clean Ni surface is known to be molecular upto fairly high temperatures. HeII spectra of CO on clean Ni shows a 1π–4σ separation of 3.0 eV. The magnitude of the 1π–4σ separation depends on the strength of bonding to the surface. On a clean Ti surface, CO has been reported to adsorb dissociatively at low temperatures [9]. We, however, find evidence for molecular adsorption at 80 K on a clean Ti surface with a large 1π–4σ separation (4.2 eV), accompanied by a small proportion of dissociatively adsorbed CO (fig. 2). We

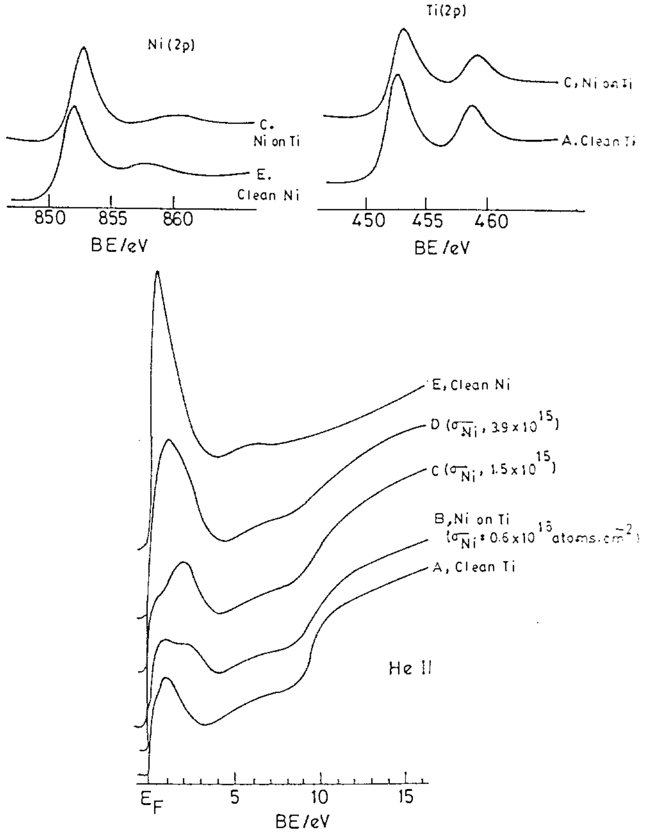

Fig. 1. HeII spectra of a Ti surface covered with Ni. Insets show Ni(2p) and Ti(2p) spectra.

feel that the HeII spectrum of CO on the clean Ti surface at 80 K corresponds closely to that of the precursor to dissociation. Accordingly, slight warming the surface to 130 K or above causes dissociation giving rise to oxidic and carbidic species with a broad feature around 6.5 eV. X-ray photoelectron spectrum in the C(1s) region (inset of fig. 2) at 80 K shows a feature due to the carbidic species at 281.2 eV in addition to that due to molecular CO at 285.1 eV; there is an additional feature at 290.2 eV possibly due to physisorbed CO$_2$ or carbonate formed by the interaction of CO with surface oxygen. The 290 eV peak intensity disappears at higher temperatures leaving only the 281 eV peak suggesting complete dissociation. The O(1s) spectra (inset of fig. 2) corroborate these conclusions. The spectrum at 80 K shows a strong peak at 530.1 eV due to molecular CO and a weaker feature at 535.6 eV due to CO$_2$/CO$_3^{2-}$. On warming the surface, we only find the peak at 529.6 eV due to the oxidic species resulting from dissociation.

HeII spectra (fig. 3) of CO adsorbed on the Ti surface covered with Ni (σNi = 1.75×10^{15} atoms/cm^2) shows the occurrence of molecular adsorption at

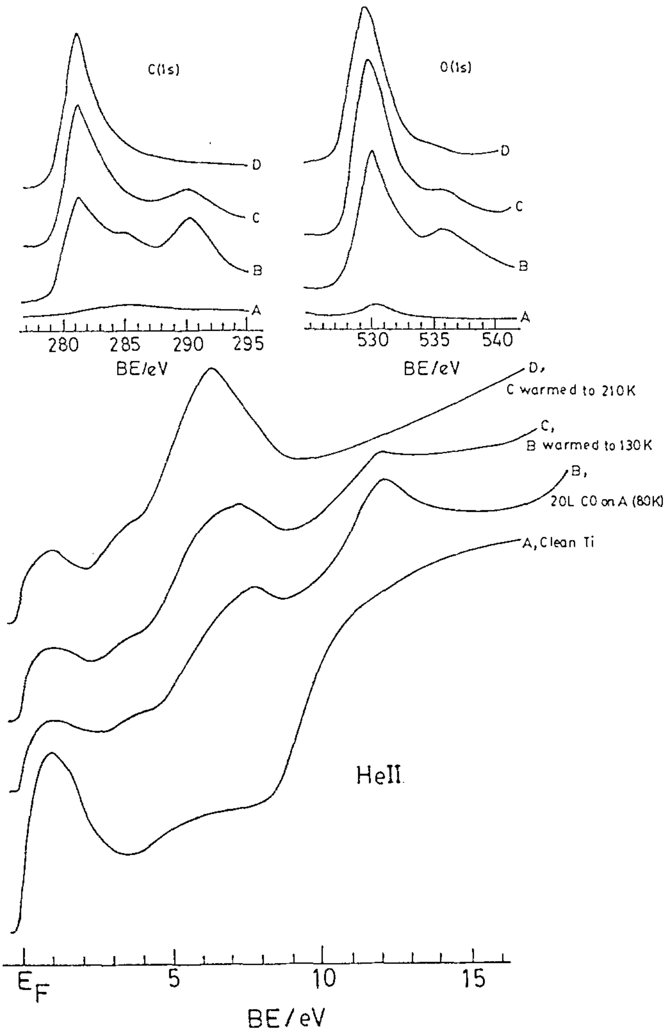

Fig. 2. HeII spectra of CO adsorbed on a clean Ti surface. Insets show (a) C(1s) and (b) O(1s) spectra.

80 K with a 1π–4σ separation of 3.3 eV. This 1π–4σ separation is in between that found on the surfaces of clean Ni (3.0 eV) and Ti (4.2 eV) showing that CO is more stable (or less strongly bound) on the modified surface than on the clean Ti surface. Evidence for partial dissociation on the Ni/Ti surface is seen at 200 K, unlike on the clean Ti surface where CO is completely dissociated at this temperature. The C (1s) spectrum at 80 K (fig. 4a) accordingly shows a prominent feature at 284.6 eV due to molecular CO on the Ni modified Ti surface and two weak features at 281.4 eV and 289.8 eV due to carbidic carbon and CO_2/CO_3^{2-} respectively. On warming the surface to 200 K, the 289.8 eV peak disappears accompanied by a decrease in the intensity of the 284.6 eV peak leaving an

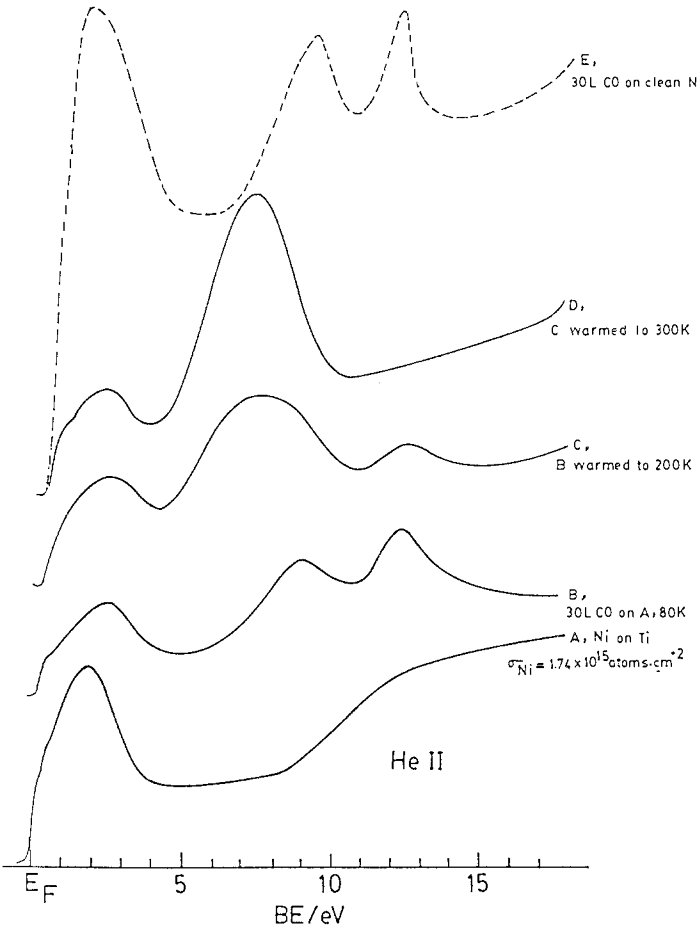

Fig. 3. HeII spectra of CO adsorbed on Ni/Ti surfaces.

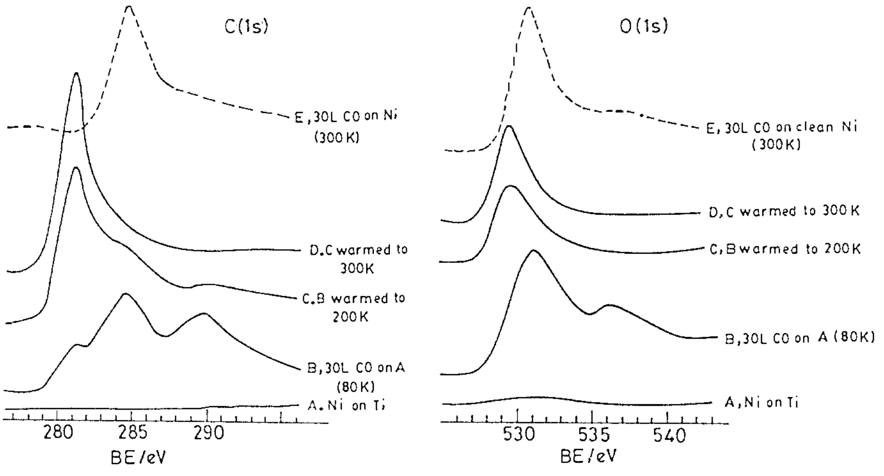

Fig. 4. XP spectra of CO adsorbed on Ni/Ti surfaces: (a) C(1s); (b) O(1s).

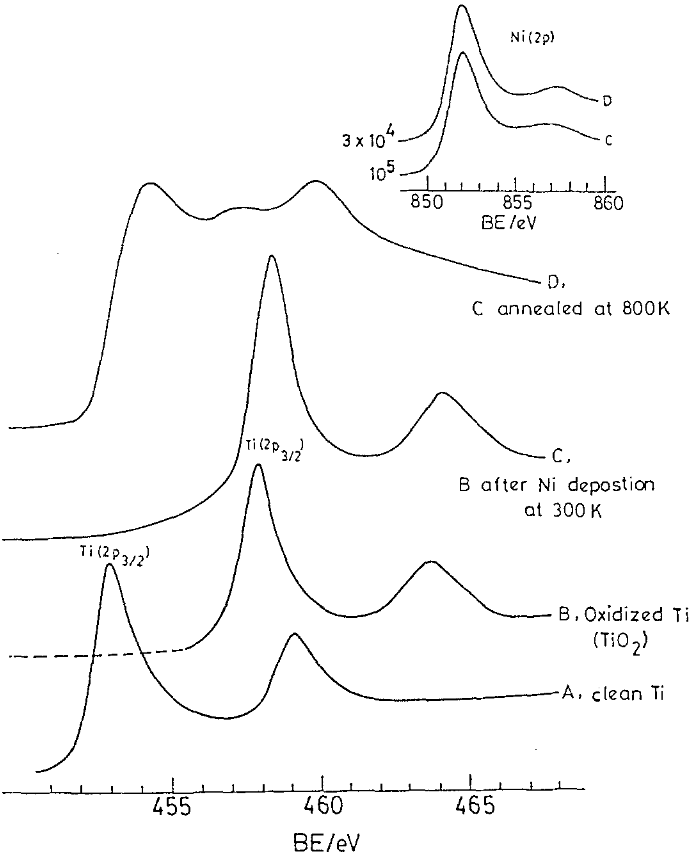

Fig. 5. Ti(2p) spectra of Ni/TiO_2 and related surfaces. Inset shows Ni(2p) spectra.

intense feature due to carbon at 281.4 eV. The 535.8 eV feature in the O(1s) spectrum (at 80 K) due to CO_2/CO_3^{2-} disappears at 200 K (fig. 4b); the peak at 531.0 eV narrows down and shifts to 529.2 eV. Thus, both the UP and the XP spectra suggest partial dissociation of CO at 200 K and complete dissociation at 300 K on the Ni/Ti surface. In an earlier study [4] on the absorption of CO on Ni-covered Al surface (σNi $= 2.4 \times 10^{15}$ atoms/cm^2), we had found molecular adsorption at 200 K, with a 1π–4σ separation of 3.5 eV; warming this surface to 300 K led to complete dissociation. It appears that dissociation of CO is more facile on the Ni/Ti surface than on the Ni/Al surface.

It is known that vacuum-annealing of TiO_2 above 670 K leads to the reduction of Ti^{4+} to Ti^{3+} [10]. The colour of TiO_2 after reduction changes from light grey to blue. In fig. 5 we show the results of annealing TiO_2 and Ni-deposited TiO_2 surfaces under UHV ($\sim 10^{-10}$ torr) at 800 K in the electron spectrometer. In the absence of Ni, only a small portion of Ti^{4+} gets reduced to Ti^{3+}, but when Ni is deposited more than 50% of the Ti^{4+} is converted to lower oxidation states, showing that the presence of Ni increases the reducibility of TiO_2. It is known

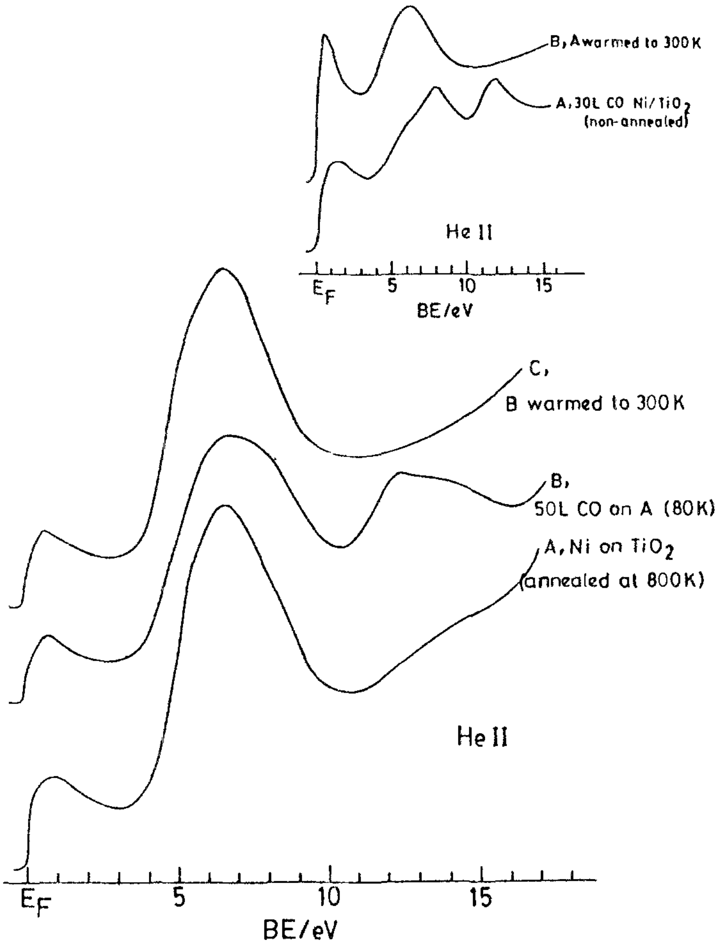

Fig. 6. HeII spectra of CO adsorbed on Ni/TiO$_2$ (annealed). Inset shows HeII spectra of CO adsorbed on Ni/TiO$_2$ (non-annealed).

that TiO$_2$ gets reduced at lower temperatures (compared to pure TiO$_2$) in the presence of Pt [11]. We see no changes in the Ni(2p) spectrum on annealing although the intensity decreases to some extent (inset of fig. 5). It seems that some of the Ni diffuses into the bulk of TiO$_2$ on annealing. The Ni coverage on TiO$_2$ before annealing was 2.8×10^{15} atoms/cm^2, but decreases to $\sim 1.5 \times 10^{15}$ atoms/cm^2 on annealing.

HeII spectra given in fig. 6 indicate that CO is dissociatively chemisorbed even at 80 K, on the annealed Ni/TiO$_2$ surface (in contrast to associative molecular adsorption found on non-annealed surfaces) indicating Ni-Ti bond formation on annealing. The spectra show the absence of peaks due to molecular CO but show the presence of a broad feature in the 12–15 eV region due to CO$_2$, CO$_3^{2-}$ etc. formed from dissociated CO. The C(1s) and O(1s) regions in XPS (see fig. 7) indicate the formation of CO$_2$/CO$_3^{2-}$ species as evidence by the features at 290.5

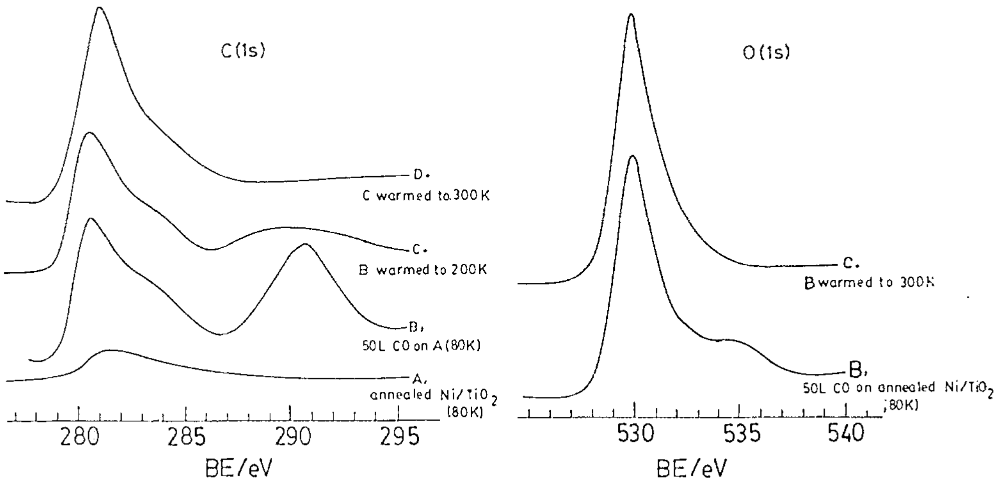

Fig. 7. XP spectra of CO adsorbed on Ni/TiO$_2$ (annealed): (a) C(1s) spectra; (b) O(1s) spectra.

eV and 535 eV respectively. The C(1s) spectrum at 80 K shows features at 280.6 eV and 283.6 eV due to carbidic species on Ti and Ni sites respectively on the surface. On warming this surface, the 290.5 eV feature disappears progressively and only the C(1s) features due to dissociated carbon remains at 300 K. The O(1s) spectrum at 300 K accordingly shows only the main peak around 530 eV due to oxidic species (fig. 7).

It is instructive to compare the adsorption of CO on the annealed Ni/TiO$_2$ surface with that on a non-annealed Ni/TiO$_2$ surface. On a non-annealed surface, we have found molecular adsorption of CO (σNi = 2.8×10^{15} atoms/cm^2) at 80 K and dissociation at 300 K. The 1π–4σ separation was 3.7 eV which is considerably higher than with clean Ni or Ni/Ti surfaces, but comparable to that found on a Ni/Al$_2$O$_3$ surface [12]. Evidence of Ni-Ti bond formation in Ni/TiO$_2$ catalysts (due to SMSI interaction) has been recently established in this laboratory by an EXAFS study [12].

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