UPS Study of the O_2, CO_2, CO and C_2H_4 Adsorption on Uranium*

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A knowledge of the chemical reactivity of uranium is needed in the study of its catalytic properties and that of its compounds, in particular the role that 5f electrons play in the interaction with reactive gases [1]. In this work, Ultra-violet and X-ray Photoelectron Spectroscopy (UPS and XPS) have been used to study the early reaction of uranium with O_2, CO_2, CO and C_2H_4. UPS is very useful because it allows the study of the evolution of the valence band region as a function of gas exposure.

Experimental

A high purity sample (<100 ppm metallic impurities) was cleaned by argon ion sputtering at 573 K and photoemission measurements were carried out with a hemispherical analyser, described elsewhere [2]. Experiments were performed in the temperature range from 73 to 573 K using a He II (40.81 eV) source for UPS.

Results and Discussion

O_2 Adsorption

UPS spectra of a clean uranium sample exposed to an increasing oxygen dosage at 73 K are shown in Fig. 1. Oxygen adsorption leads to the growth of two peaks at about 2 and 6 eV binding energy (BE), also
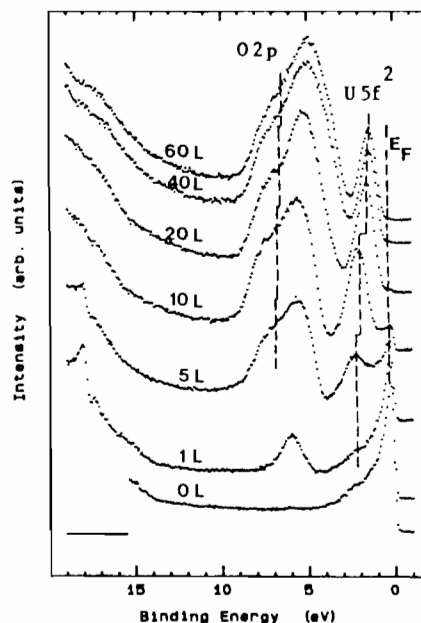

Fig. 1. UPS study of the O_2 adsorption on U at 73 K.

found in UO_2 [3], and attributed to the O2p band and the localized $U5f^2$ level of uranium oxide. The emission at the Fermi level (E_F) becomes smaller as the oxide band grows, indicating a decrease in the uranium metal concentration. At low surface coverage, the O2p peak is symmetrical (peak I) and above 3 L (L = Langmuir) a second peak appears (II) on the high binding energy side; the combination of the two forms the O2p band for UO_2. The intensities of the O2p band (I and II), the $U5f^2$ and the emission at E_F hence vary with O_2 dosage. Up to 8 L exposure all spectral features vary linearly, pointing to a constant sticking probability. At 14 L, the O2p area reaches a 'plateau', while the $U5f^2$ area passes through a maximum. At 20 L, the O2p area increases again, while the $U5f^2$ area decreases and the intensity at E_F becomes zero. Line I and the $U5f^2$ peak both shift to lower binding energy (0.2 eV) with increasing surface exposure. The energy difference between these two peaks remains constant for all temperatures and exposures. At 300 K, O_2 adsorption again induces the O2p and $U5f^2$ lines and the suppression of the emission at E_F. Above 4 L, the O2p line has two components (I and II), which are better resolved than for the 73 K adsorption. The exposure-dependent shift (0.7 eV) of peak I and the $U5f^2$ emission to lower binding energy are less marked than at 73 K.

At 73 and 300 K, initial oxygen adsorption takes place with constant sticking probability up to about 70% of the saturation intensity; the former corresponds to one monolayer of uranium oxide. This

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constant sticking probability up to total coverage implies the existence of a precursor state of O_2, either physisorbed or chemisorbed oxygen. The binding energy of the $U5f^2$ peak at low oxygen coverage is 2.1, 2.3 and 2.5 eV for the 73, 300 and 573 K adsorptions, respectively. At high surface coverage (>10 L) for 300 and 573 K the BE stays at its initial value, but at 73 K it shifts toward 1.4 eV, where it is also found for stoichiometric UO_2 and higher oxides [4]. Because the BE shift is the same for the $U5f^2$ and the $O2p$ peaks, this can only be due to a change in the surface potential produced either by oxygen chemisorption at 73 K, or by a change in the oxide stoichiometry. We have followed the change of the $U5f^2/O2p$ area ratio with oxygen exposure to provide an indication of the type of oxide being formed (Fig. 2). At low surface coverage the ratio is high (4.8) but decreases to a constant final value of 2.8 at 300 and 573 K. However, at 73 K it increases to a value of about 6 at exposures higher than 12 L. We believe that at low surface exposure (<7 L), dissociative O_2 chemisorption occurs with a local U—O interaction ('surface state'), resulting in a symmetrical $O2p$ line (line I, Fig. 1). There is no oxide phase and the $U5f^2$ oxide-induced peak and line II are missing. At low coverage the ratio has its highest value of 4.8 at 73 K because of the low oxygen mobility, which precludes the formation of the thermodynamically stable oxide phase. At 573 K, even at low exposures (<3 L), line I and II are present and, accordingly, the $U5f^2$ peak is more pronounced than at lower temperatures. Further O_2 adsorption at 300 and 573 K leads to the growth of the $U5f^2$ peak and to $O2p/U5f^2$ ratio of 2.8, which we assign to that of substoichiometric UO_2 by comparison to data from sputtered and
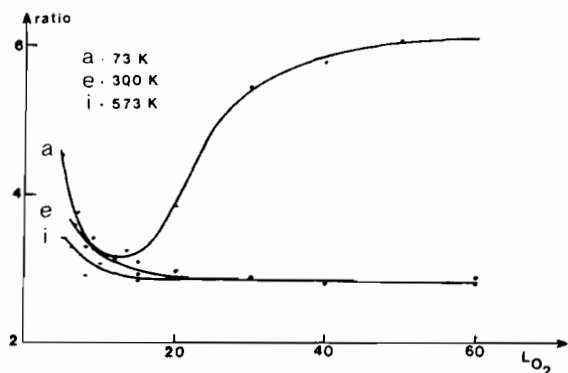

Fig. 2. $O2p/U5f^2$ ratio as a function of coverage and temperature.

scraped $UO_{2.0}$. Moreover, the increase of the $O2p/U5f^2$ ratio to a value of 6 coincides with the shift of the $U5f^2$ peak to a value of 1.4 eV.

CO, CO_2 and C_2H_4 Adsorption

Both CO and CO_2 adsorb only dissociatively at low coverage, even at 73 K, where the probability of non-dissociative adsorption is highest. This is shown by the growth of the $O2p$ oxide line and the absence of any molecular emission. At high surface coverage, physisorption leads to the appearance of molecular emission lines with the same BE as for gas molecules. Because the emission at E_F only decreases slightly, the surface oxide layer at saturation must be very thin (<1 monolayer). At 300 and 573 K, saturation at one monolayer takes place again but, as expected, CO or CO_2 do not physisorb. O_2 adsorption on the saturated surface produced by CO or CO_2 adsorption leads to further surface oxidation and the disappearance of the Fermi level emission. This means that the self-limiting surface oxidation with CO or CO_2 is not due to the inhibition of oxygen bulk diffusion by a carbide layer, but to the non-dissociation of CO on a completely oxidized surface. The $U5f^2$ oxide peak at CO or CO_2 saturation is very small, showing that a surface oxide barely forms. C_2H_4 adsorption at 573 K should lead to the formation of a surface carbide, as is the case for many other metals [5]. Our data showing a peak at 4 eV and an emission at E_F are in disagreement with published UC spectra [6], which have peaks at 2 and 6 eV and no Fermi level emission. However, the peak at 4 eV BE is present in numerous transition metal carbides and is commonly assigned to the C2p band. On the other hand, UC has metallic properties and theoretical band structure calculations [7] report a density of states at E_F, which is clearly shown in our measurements.

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