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REDUCTIVE COUPLING OF CARBON MONOXIDE MOLECULES OVER OXYGEN DEFECTED UO_2 (111) SINGLE CRYSTAL AND THIN FILM SURFACES

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Coupling reactions of chemical compounds have a unique place in chemistry because they represent a key step in building complex molecules from simple ones. Solid catalysts are often used to accelerate the reaction rate by stabilizing the reaction intermediate, and can thus enhance or initiate a reaction that often could not be conducted in their absence. Among the most challenging coupling reactions is the selective coupling of two carbon monoxide molecules to C_2 compounds. This rare reaction, which has been previously observed in organometallic chemistry (solution chemistry), was successfully conducted on oxygen-defected uranium dioxide single crystal and thin-film surfaces. The oxidation/reduction reactions over the O-defected surfaces were studied using high-resolution x-ray photoelectron spectroscopy. This method revealed the reaction pathway.

The surface reaction of the oxide of actinides, such as uranium oxides, is one of the least studied, yet one of the most fascinating. Our interest in this surface reaction started a decade ago. The reaction represents one of the most challenging systems among all chemical reactions of solids. The *f*-orbitals of the actinide elements, because they differ in symmetry from the *d*-orbitals, can adsorb a reactant in a unique configuration and thus may orient to different chemical pathways not seen on the surfaces of early transition metals. In addition, relativistic effects, due to the large size of the nucleus, result in a wide range of oxidation

states of metal cations, making them very active but also unstable. The observation of this reaction on a solid surface has allowed the use of x-ray photoelectron spectroscopy (XPS) (**Figure 1**). However, conventional XPS was not adequate to carry out accurate qualitative and quantitative investigations because of inevitable oxidations, over time, of the surface U atoms during data collection. By using the high-intensity, high-resolution (HR), and fast acquisition time available on NSLS beamline U12A, it was possible to study the mechanism of this reaction and outline quantitatively the changes in surface oxidation states before and after the reaction.



Authors (top) Hicham Idriss and Sanjaya Senanayake

Figure 2 shows the HRXPS spectra of the U4f and O1s lines of the clean oxygen-defected UO_2 thin-film surface, as well as the same surface upon exposure to carbon monoxide. The main lines at 380 and 391 eV are due to $\text{U}4f_{7/2,5/2}$ of U^{4+} while the shoulder at the low binding energy side of the $\text{U}4f_{7/2}$ is exclusively due to U cations in lower oxidation states than +4 (a detailed study of this region has been conducted in a separate work). Upon adsorption of carbon monoxide (b) the intensity of this shoulder decreases and becomes negligible at surface saturation (c and d). This is because CO has donated its oxygen atom to surface defects. A similar observation is seen in the O1s region. Detailed analysis of the C1s region has shown that the dissociation is not total. Parallel work has shown the formation of acetylene and ethylene as the end product at 550 K and above.

The above three observations — oxidation upon adsorption, partial dissociation at room temperature, and desorption of C_2 compounds at high temperature — can be explained in **Scheme 1**.

In **Scheme 1**, the η^2 - η^2 -bis-formyl species is proposed to be formed on a U surface; this could only be accommodated because of the particular symmetry of the *fx*² orbitals. The bis-formyl species react at room temperature to give the pinacolates; this in turn gives $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ at high temperatures.

Although the above reaction is not catalytic, its observation may open the routes for the design of new catalytic materials using uranium oxides or oxides of similar properties.

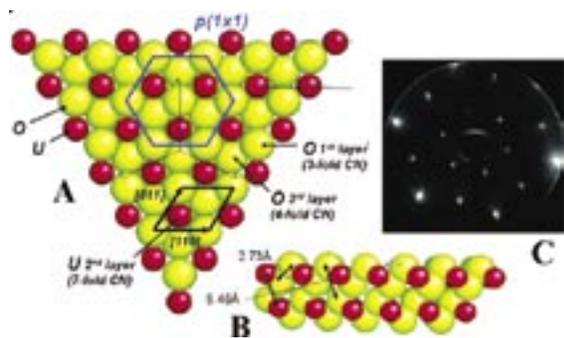


Figure 1. Ball model of the $\text{UO}_2(111)$ surface showing the hexagonal arrangement of U and O atoms and lattice parameters. Red balls are U atoms and yellow balls are O atoms (A: top view, B: side view). C: Low Energy Electron Diffraction (LEED) of the $\text{UO}_2(111)$ surface showing the extended order (131 eV). The surface is entirely composed of oxygen atoms. Their partial removal makes the U atoms (initially in the second layer) highly reactive for both reduction and coupling reactions.

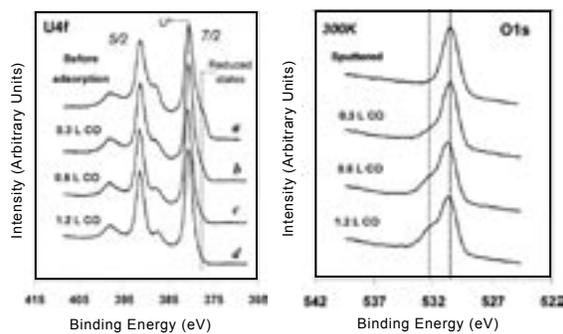
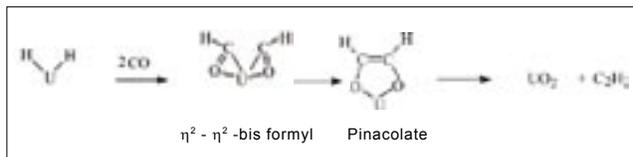


Figure 2. HRXPS U4f and O1s lines of Ar-ion sputtered UO_2 thin film before (a) and after (b, c, and d) reacting with CO at the indicated exposures in Langmuir ($L = 10^{-6}$ torr s).



Scheme 1