# Carbon monoxide reaction with $UO_2(111)$ single crystal surfaces: A theoretical and experimental study

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The reaction of CO has been investigated on the surfaces of  $UO_2(111)$  single crystal. Over the stoichiometric surface CO does not adsorb at 300 K and no further reaction is noticed. Over  $UO_{2-x}$  (prepared by Ar<sup>+</sup> bombardment), CO molecules adsorb and in presence of traces of H<sub>2</sub> they couple to form acetylene molecules that desorb in two temperature domains during temperature programmed desorption (TPD). In the presence of excess H<sub>2</sub> the coupling product is found to be ethylene. X-ray photoelectron spectroscopy (XPS) of the core level shows the presence of an U 4*f* line at 377 eV on the  $UO_{2-x}$  surface, attributed to U metal. This line disappears upon CO adsorption (5 L and above) at 300 K; indicating oxidation of U metal atoms by O from dissociatively adsorbed CO. XPS C 1*s* shows that the only C containing species formed is carbide. Computation of a  $\alpha$ -U metal 2d-periodic slab was also conducted using plane-wave pseudopotential in the density functional theoretical framework. Two modes of CO adsorption were considered: molecular and dissociative. The dissociative adsorption was found more energetically favoured by 0.46 eV. From TPD, XPS and computation results it is strongly suggested that CO is dissociatively adsorbed on  $UO_{2-x}$  and that a stable U–C species is formed at 300 K. © 2005 American Vacuum Society. [DOI: 10.1116/1.1881637]

#### I. INTRODUCTION

The surface chemistry of the uranium oxide system is very rich. The fact that uranium ions can accommodate several coordination numbers and several oxidation states makes them very active for oxidation/reduction reactions. For example,  $\beta$ -UO<sub>3</sub> has been shown active for the oxidative coupling of two molecules of acetylene<sup>1</sup> or ethylene<sup>2</sup> to make furan (C<sub>4</sub>H<sub>4</sub>O). Two reasons are behind this coupling reaction: the ease by which oxygen transfer occurs, from the lattice to the adsorbate, and the possibility of accommodating two adsorbates on one uranium center favoring their coupling. A similar reaction also occurs on the more reduced form of the oxide; reductive coupling of carbonyl compounds. UO<sub>2</sub> and UO<sub>2-x</sub> are active for the reductive coupling of formaldehyde<sup>3</sup> and acetaldehyde<sup>4</sup> to ethylene and butenes, respectively. In this reaction the driving force is the accommodation of extra oxygen atoms in the lattice (forming  $UO_{2+x}$ ). In both reactions the key point for coupling is the high coordination number of U atoms that allows a close interaction of two adsorbates to couple together. UO<sub>2</sub>, having the fluorite structure, has a tendency to accommodate extra oxygen, up to  $UO_{2.25}$ . The change of  $UO_2$  from  $UO_{2-x}$  (defected and *n*-type semiconductor) to  $UO_{2+x}$  (*p*-type semiconductor) has been studied by x-ray photoelectron spectroscopy  $(XPS)^{5}$  and ultraviolet photoelectron spectroscopy,<sup>6</sup> and the

shift in the core level position was due to the change in the semiconducting properties (from n type to p type).

CO reactions, over oxide surfaces, have been studied in detail for long years. The most common chemical reaction studied for CO is its oxidation to  $CO_2$ . In that regard  $U_3O_8$  is a very active catalytic material, far superior to most early transition metal oxides.<sup>7,8</sup> Far less work has been reported for the reduction (including coupling) of CO on oxides. Although no surface science work has yet addressed the coupling of CO molecules to higher hydrocarbons, examples of coupling of CO in coordination chemistry are common. On U complexes coupling of two molecules of CO to enolates has been reported a while ago.9 Other metals, such as V, Mo, and W,<sup>10</sup> are also active for this reaction. In this work we show that one can selectively make C2H2 from CO and H2 over the surface of a  $UO_{2-x}(111)$  single crystal. The oxidation/reduction of  $UO_{2-x}$  was followed by the U and O core levels while the reaction products were monitored by temperature programmed desorption (TPD). In order to complement the experimental work computation of a U metal surface ( $\alpha$ -U) slab vis a vis CO adsorption was conducted using the *ab initio* density functional theory (DFT) pseudopotential method with a plane wave basis set. Both molecular and dissociative modes of CO adsorption were considered and the results are compared to the experimental study.

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FIG. 1.  $(2 \times 1)$  surface unit cell of  $\alpha$ -uranium (001) slab.

# **II. EXPERIMENT**

## A. Ultrahigh vacuum study

The experiments undertaken for this work were performed in two Ultrahigh vacuum (UHV) (pressure  $\approx 1$  $\times 10^{-10}$  Torr) stainless steel chambers. Both chambers have previously been described elsewhere.<sup>3,5</sup> The surface was prepared prior to all experimentation with several cycles of annealing to 800 K and Ar<sup>+</sup> sputtering (3.5 kV, 18 mA,  $P_{Ar}$ =  $1 \times 10^{-5}$  Torr in one chamber and 4 kV and 20 mA,  $P_{Ar}$  $=5 \times 10^{-5}$  Torr in the other one), and further confirmed for stoichiometry (or near stoichiometry) using XPS and low energy-electron diffraction with a sharp hexagonal structure as presented in previous works.<sup>3,5</sup> The defected surface  $(UO_{2-r})$  is obtained with extended periods of Ar<sup>+</sup> sputtering and analysed by XPS. The surface is annealed to 370 K to remove weakly adsorbed argon atoms after sputtering and before dosing. High purity carbon monoxide gas (99.9%) was obtained from Matheson Gas Products Inc. (G1918755) and introduced to the UHV chamber for adsorption at room temperature, using a stainless steel dosing arm pumped (1  $\times 10^{-5}$  Torr) with a diffusion pump, by way of a precision leak valve and dosing needle (1/16 in.). XPS measurements are undertaken using Al  $K\alpha$  radiation (1486 eV), at 240 W and 13.8 kV accelerator voltage; with up to 15 coadded scans to optimise signal for U 4f and O 1s and to 20 coadded scan for C 1s. Pass energy was 25 eV for U 4f and O 1s and 50 eV for C 1s. Scanning was conducted at a step rate of  $0.1 \text{ eV s}^{-1}$  with 300 ms per step.

#### **B.** Computation

All calculations have been performed in the DFT framework using the generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional.<sup>11</sup> We have employed the pseudopotential method with ultrasoft pseudopotentials<sup>12</sup> which allowed using a plane-wave basis set with a kinetic-energy cutoff of 40 Ry, far lower than the conventional norm-conserving type.<sup>13</sup> The electronic configuration of uranium metal is [Rn]  $6d^15f^37s^2$ . The uranium pseudopotential was created from a scalar-relativistic all-electron calculation of an ionized configuration ([Rn]  $6d^15f^37s^0$ ) similar to the potential used by Crocombette *et al.*<sup>14</sup> but using the Vanderbilt ultrasoft pseudopotential generation scheme with two projectors for each angular momentum (*s*, *p*, *d*, *f*) and using the PBE<sup>11</sup> gradient corrected exchange and correlation functionals.

Brillouin zone integrations have been performed with the Marzari–Vanderbilt spreading technique,<sup>15</sup> using a smearing parameter of 0.015 Ry and a  $5 \times 5 \times 1$  Monkhorst–Pack<sup>16</sup> k points. All calculations have been performed using the *PWscf* version 2.0.3 package.<sup>17</sup>

The (001) surface of  $\alpha$ -U is modeled using periodic supercells. It has been shown that the surface energy for the metal actinide Pu is rapidly converging with film thickness.<sup>18,19</sup> In Ref. 18 the surface energy of Pu metal decreased by 16% from one to two layers and by 9% for an additional third layer. After three layers thickness the surface did not change (0.78 eV). In the case of  $\alpha$  uranium metal the unit cell is composed of four U atoms with their interatomic distances presented in Fig. 1. We have opted for two layers because of computational limitations. The two atomic layers used in the calculations representing a two-dimensional (2 × 1) surface unit cell is also shown in Fig. 1.

For consistency, calculations for the gas-phase CO molecule have been carried out using the same supercell approach used for the slab studies. As generally found in DFT calculations, the structural properties are relatively well described. The CO molecule was placed in the middle of a supercell (dimension  $8 \times 8 \times 8$  Å). The calculated bond 1080 Senanayake et al.: Carbon monoxide reaction with UO<sub>2</sub>(111) single crystal



FIG. 2. Dissociative CO adsorption [(a) and (b)]; molecular CO adsorption [(c) and (d)]; (a) and (c) side view; (b) and (d) top view.

length of CO (1.14 Å) is well represented and is in good agreement with the experimental value of 1.13 Å.

To study CO adsorption, a layer (corresponding to  $\theta$  =0.25) of CO was modeled on the top-surface of the slab [see Figs. 2(a)–2(d)], with the (001) slab constrained at experimental bulk values. Only the CO molecule was allowed to relax. A vacuum layer equivalent to five atomic layers (11.82 Å) was employed to largely reduce spurious interactions between image slabs.

The chemisorption energies  $E_{\text{chem}}$  are referred to the clean  $\alpha$ -uranium (001) surface and the isolated adsorbate molecule

$$E_{\text{chem}} = [E_{\text{system}} - (E_{\text{slab}} + E_{\text{adsorbate}})], \qquad (1)$$

where the total energy of the adsorbate-substrate system, of the clean stoichiometric surface, and of the free adsorbate molecule in gas phase are represented by  $E_{\text{system}}$ ,  $E_{\text{slab}}$ , and  $E_{\text{adsorbate}}$ , respectively. By this definition, stable adsorbates will have negative chemisorption energies.

The surface energy,  $E_{suf}$  of  $(001)\alpha$ -uranium was calculated using the following equation:

$$E_{\rm suf} = [E_{\rm slab} - N \times E_{\rm bulk}]/2A, \tag{2}$$

where  $E_{\text{slab}}$  is the total energy of the (001) slab and  $E_{\text{bulk}}$  is the energy of the bulk per uranium atom. *N* is defined as the total number of uranium atoms in the slab and *A* is unit surface area, which was found to be  $33.278 \times 10^{-20} \text{ m}^2$ .

Considering the errors in the structural relaxation and the energy convergence with respect to the planewave cutoff energy and  $\mathbf{k}$ -point mesh, we estimate an overall numerical accuracy for the chemisorption energies of about 1 mRy. Table I summarizes the various tests of convergence.

# **III. RESULTS**

The results will be presented as follows. First, TPD of CO on  $UO_{2-x}$  will be shown indicating desorption of  $C_2H_2$  and  $C_2H_4$ . The presence of U metallic uranium atoms in addition

to U<sup>4+</sup> on UO<sub>2-x</sub> surface and near surface is shown by their XPS core levels and compared to those of the stoichiometric UO<sub>2</sub>(111) single crystal. *Ab initio* DFT computational results will be presented next showing that the preferential mode of adsorption for CO on the  $\alpha$ -U surface is dissociative.

#### A. Temperature programmed desorption of CO

 $UO_2$  was sputtered with Ar<sup>+</sup> ions for  $\frac{1}{2}$  h, followed by a flash to 373 K to remove loosely bonded Ar atoms. This was followed by a control experiment in which a TPD is conducted. Mass signals due to Ar and traces of H<sub>2</sub>O were detected but no carbon containing species was seen to desorb indicating that the sputter line was carbon free. The same experiment was conducted thus after dosing of CO at 300 K. Several exposures were conducted from 1 to 9 L. Figure 3 shows desorption of products monitored during TPD after a 9 L dosing. The striking result is the formation of acetylene  $(m/e \ 25, \text{ and } 26)$ . Acetylene formation is due to coupling of two molecules of CO and their association with the inevitable traces of H<sub>2</sub> in the background of the chamber (as well as during sputtering). Figure 4 shows the results of the same procedure but this time with dosing CO and H<sub>2</sub> with a 1 to 1 ratio (CO prepared in the dosing line). The coupling product is still present but has mainly shifted to ethylene instead of acetylene.

Considerable amounts of  $CO_2$  are formed when CO is dosed alone or in addition to  $H_2$ . Repeating the CO–TPD

TABLE I. Convergence of total energy per uranium atom as a function of kinetic cutoff energy and k points.

Kinetic cutoff energy (Ry)	30	40	45
Total energy per uranium atom/Ry	-103.586 48	$-103.593\ 00$	-103.597 85
<i>k</i> -point scheme (Monkhorst-Pack)	3×3×1	$5 \times 5 \times 1$	7×7×1
Total energy per uranium atom/Ry	-103.534 84	$-103.536\ 46$	-103.536 61



FIG. 3. TPD of CO (and traces of H<sub>2</sub>) over Ar<sup>+</sup>-sputtered UO<sub>2</sub>(UO<sub>2-x</sub>)  $\times$ (111) single crystal. CO exposure 9 L at 300 K.

experiments after different sputtering time shows that the amount of  $CO_2$  increases with increasing reduction, together with increasing conversion of the reactant (CC). This result may indicate an additional route for CO oxidation on defected surfaces; Boudouard reaction  $[2 CO(a) \rightarrow CO_2(g) + C(a); (a)$  for adsorbed, (g) for gas] is a likely pathway



FIG. 4. TPD of CO and  $H_2$  (molar ratio 1 to 1) over Ar<sup>+</sup>-sputtered  $UO_2(UO_{2-x})$  single crystal. CO exposure 5 L at 300 K.



FIG. 5. CO,  $CO_2$ , and acetylene fractional yield during CO–TPD as a function of sputtering time.

explaining this trend. On the other hand, the yield for  $C_2H_2$  remains constant (within few percent), Fig. 5.

### B. XPS after CO adsorption at 300 K

Figure 6 shows the XPS U 4*f* region for the stoichiometric UO<sub>2</sub>(111) single crystal, the one after Ar<sup>+</sup> sputtering and that after CO dosing on the Ar<sup>+</sup> sputtering. Details of the peak positions are given in Table II. In a recent work we have studied in details XPS U 4*f* region of stoichiometric. O<sub>2</sub>-annealed and Ar-sputtered UO<sub>2</sub>(111) single crystal.<sup>5</sup> The O<sub>2</sub>-annealed surface is a *p*-type semiconductor while the O-defected surface is a *n*-type semiconductor. Consequently the U 4*f* XPS lines for U<sup>4+</sup> states move to higher binding



FIG. 6. XPS U 4*f* of UO<sub>2</sub>(111) single crystal, Ar<sup>+</sup>-sputtered UO<sub>2</sub>(UO<sub>2-x</sub>)  $\times$ (111) single crystal and CO dosed (5 L)Ar<sup>+</sup>-sputtered UO<sub>2</sub>(UO<sub>2-x</sub>)(111) single crystal at 300 K.

TABLE II. XPS U 4*f* and O 1*s* binding energy for UO<sub>2</sub>(111) single crystal,  $UO_{2-x}$  (Ar<sup>+</sup> sputtered), and  $UO_{2-x}$  after 5 L exposure to CO at 300 K.

	UO <sub>2</sub> /eV	$UO_{2-x}$ (Ar <sup>+</sup> sputtered)/eV	$UO_{2-x}+CO/eV$
$U^{4+}4f_{7/2}$	380.0	380.8	380.5
Satellite	387.0		387.7
$U^{4+}4f_{5/2}$	390.9	391.6	391.5
Satellite	397.8	398.6	398.4
$U^{x+}4f_{7/2}$		377.2	
$U^{x+}4f_{5/2}$		388.1	
O 1s	530.6	531.3	531.0

energy (due to the shift in the Fermi level) for the O-defected surfaces. This movement is also seen in the U 5f valence level. The clean UHV-annealed surface of  $UO_2(111)$  is used as the reference. The XPS U 4f line for stoichiometric  $UO_2$ has been seen by numerous authors and should be at 380.0 (+/-0.1) eV.<sup>20,21</sup> In our case it was at 378.7 eV; all U 4f spectra are thus shifted by 1.3 eV. In Fig. 6 the appearance of lines at about 377 eV is clear. This broad shoulder is due to U metal (and plausibly U atoms in an intermediate oxidation state,  $(0 < U^{4x+1} < U^{4+})$ . We have recently investigated by synchrotron radiation this region on a sputtered thin film of UO<sub>2</sub>; it is clear that this region is composed of more than one oxidation state.<sup>22</sup> The shift of the U<sup>4+</sup> towards higher binding energy is not due to charging but is a reproducible shift that has been studied by us and other workers in some details.<sup>5,6</sup> It is due to the formation of the n-type semiconductor (shifting of the Fermi level away from the valence band). Upon adsorption of CO molecules (5 L) most of the line attributed to the U metal has disappeared. The most plausible explanation is that dissociative adsorption of CO on the U metals has occurred and may have resulted in the formation of U-C bonds. The C 1s region does show that the C is present on the surface in a carbide form; a peak with a binding energy of 281.5 eV, Fig. 7. Due to limitation of our instrument resolution it was not possible to distinguish the O deposited from CO dissociation from that of the lattice oxygen.

## C. Computation

## 1. The α-U slab

We have opted to study the computation over U metal because it was clear that the U metal phase is behind the adsorption and reaction of CO to  $C_2H_2(C_2H_4)$ . Ideally one would compute the UO<sub>2</sub> system, with defect formation in due course, then study the interaction of CO with these defects. This approach was judged far more difficult in particular because of the hybridisation between the U 5*f* and O 2*p* electrons and should the subject of a devoted study. It is worth indicating that to date there has only been one ab initio calculation for surface reaction of UO<sub>2</sub>.<sup>23</sup>

The  $\alpha$ -U phase was chosen for this study as it was found to be the most energetically favorable phase, amid others.<sup>24</sup> The computed surface energy was found equal to 0.67 J m<sup>-2</sup>; for example the surface energy of Al(100) is 0.92 J m<sup>-2</sup>.<sup>25</sup>

#### 2. α-U+CO(θ=0.25)

Adsorption of CO was conducted at submonolayer coverage. Two types of adsorption were studied: molecular and dissociative. Figures 2(a)–2(d) show the converged geometries of the two modes of adsorption. Molecular adsorption is far weaker than the dissociative one (by 0.46 eV). The dissociative adsorption has resulted in O and C atoms, each threefold coordinated to U atoms. The details of both converged geometries are summarized in Table III. The distance between U and O of ~2.20 Å close to that of  $UO_2(2.37 \text{ Å})^{26}$ while that between U and C atoms is ~2.23 Å. The U to C distance in UC is equal to 2.48 Å, in UC<sub>2</sub> it is between 2.32 and 2.57 Å, and in U<sub>2</sub>C<sub>3</sub> it is between 2.46 and 2.76 Å.<sup>27</sup>

Binding energies. The molecular binding energy of CO on  $\alpha$ -uranium (001) was found to be -2.07 eV as compared to the dissociative binding energy of CO on the same surface



FIG. 7. XPS O(1s) of UO<sub>2</sub>(111) single crystal, Ar<sup>+</sup>-sputtered UO<sub>2</sub>(UO<sub>2-x</sub>)  $\times$ (111) single crystal and CO dosed (5 L)Ar<sup>+</sup>-sputtered UO<sub>2</sub>(UO<sub>2-x</sub>)(111) single crystal. XPS O1s of CO dosed (5 L)Ar<sup>+</sup>-sputtered UO<sub>2</sub>(111)(UO<sub>2-x</sub>) single crystal at 300 K.

TABLE III. Interatomic distances for both dissociative and molecular CO adsorption geometries.

Interatomic distance/Å	Dissociative adsorption	Molecular adsorption
C-U1	2.03	2.50
C-U3	2.28	2.15
C-U4	2.28	
O-U1	2.11	2.45
O-U3	2.30	
O-U4	2.30	
O-U2		2.45
C-0	2.58	1.32

which is -2.53 eV. There is no reported literature for the binding energy of CO on U metal either experimentally or by computational methods. The number is however within an accepted value for metals.

#### **IV. DISCUSSION**

The formation of  $C_2H_2$  from CO can be represented by several chemical equation the most realistic of them are the following two:

4 CO + H<sub>2</sub>  $\rightarrow$  C<sub>2</sub>H<sub>2</sub> + 2CO<sub>2</sub>  $\Delta G = -29 \text{ kJ mol}^{-1}$ , (3)

$$2 \text{ CO} + 3\text{H}_2 \rightarrow \text{C}_2\text{H}_2 + 2\text{H}_2\text{O}$$
  $\Delta G = +28 \text{ kJ mol}^{-1}$ . (4)

Clearly  $\Delta G$  favors Eq. (3). In addition, considerable amount of CO<sub>2</sub> is seen during TPD while only traces of H<sub>2</sub>O desorbed. It is, however, not clear if all CO<sub>2</sub> is formed from CO, some might be due to CO oxidation with loosely bonded lattice O atoms formed upon sputtering. CO<sub>2</sub> can also be formed from CO following Boudouard reaction<sup>28</sup> and this may explain the increase of CO<sub>2</sub> yield with increasing sputtering time (increasing the amount of U metals on the surface) as seen in Fig. 5.

One plausible way of making acetylene is via the initial formation of uranium carbide UC and/or  $UC_2$ :

2 CO + 2 U 
$$\rightarrow$$
 UO<sub>2</sub> + UC<sub>2</sub>  $\Delta G = -844.4 \text{ kJ mol}^{-1},$ 
(3a)

$$2CO + U \rightarrow UC + CO_2 \quad \Delta G = -206 \text{ kJ mol}^{-1}.$$
(3b)

The heats of formation of UC<sub>2</sub> and UC are very similar (few kJ mol<sup>-1</sup> within experimental errors) and for the purpose of the earlier calculation we have taken them as equal to  $-87 \text{ kJ mol}^{-1}$ .<sup>29</sup> Although these equations are very exothermic what happens after is not clear. Hydrogenation of UC<sub>2</sub> to acetylene and/or ethylene is very endothermic and is unlikely to occur unless coupled via some common intermediates. Water (present as traces in the chamber particularly during sputtering) might be another reactant forming ethylene from UC or UC<sub>2</sub>:

$$UC_2 + 2H_2O \rightarrow UO_2 + C_2H_4 \qquad \Delta G = -402 \text{ kJ mol}^{-1}.$$
(5)

The contribution of the above reaction is to be taken with some reservation since acetylene is formed with large amounts in the absence of  $H_2$  and not ethylene.

There is the possible formation of UO instead of  $UO_2(UC_2+H_2O \rightarrow UO+C_2H_2)$  but there is no (yet) spectroscopic evidence for the existence of  $U^{2+}$ .

The adsorption of CO on U metal has been investigated previously by other workers and the mode was found dissociative at low coverage even at 100 K.<sup>28</sup> It is also important to note that CO reaction with U and Th metals in the gas phase is dissociative.<sup>30</sup> The thermodynamics for making UC<sub>2</sub> from CO favors this dissociative mode. Our XPS results clearly show that the same mode of adsorption occurs on  $UO_{2-x}$ 

 $(Ar^+$ -sputtered UO<sub>2</sub>) surfaces by XPS. The complementary DFT computation also shows that on U metal the dissociative mode is favoured. The exact reaction mechanism for making C<sub>2</sub>H<sub>2</sub> is not clear. The earlier equations describe initial and final states that may or may not be reaction intermediate.

The UC<sub>2</sub>, species as a reaction intermediate, is not in line with a pinacol route (to make the coupling reaction as seen in organometallic U and Th based compounds,<sup>9</sup> since a C2 diol species should give XPS C 1*s* lines close to 286.5 eV (not observed)

$$2 \operatorname{CO}(a) + 2 \operatorname{H}(a) + U(s) \longrightarrow UO_2 + C_2 \operatorname{H}_2$$

However a more detailed study particularly at low dosing temperatures is needed to further understand the reaction.

#### **V. CONCLUSIONS**

The rich chemistry of uranium oxide system can serve as a model for studying chemical reactions in general and coupling reactions in particular. The work shows that while  $UO_2(111)$  single crystal is inactive for CO coupling, creating oxygen defects results into coupling of CO molecules to acetylene and ethylene. This coupling reaction appears to occur after dissociative adsorption of CO upon adsorption at 300 K. This dissociative adsorption results in oxidation of U

metal and the formation of U carbide and U oxide. The stable threefold oxygen and threefold carbon species upon dissociative adsorption of CO, computed by ab initio DFT are more favored than the molecularly adsorbed CO on U by 0.46 eV. Concomitant with C2 desorption during TPD a considerable formation of  $CO_2$  is also noticed. Although the exact reaction mechanism for the formation of  $C_2$  hydrocarbons and  $CO_2$  is not clear, both reactions (acetylene and  $CO_2$  formation) appear coupled.

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- <sup>1</sup>H. Madhavaram and H. Idriss, J. Catal. **206**, 155 (2002).
- <sup>2</sup>H. Madhavaram and H. Idriss, Stud. Surf. Sci. Catal. **110**, 265 (1997).
- <sup>3</sup>S. D. Senanayake, S. V. Chong, and H. Idriss, Catal. Today 85, 311 (2003).
- <sup>4</sup>S. V. Chong and H. Idriss, J. Vac. Sci. Technol. A 19, 1933 (2001).
- <sup>5</sup>S. D. Senanayake and H. Idriss, Surf. Sci. **563**, 135 (2004).
- <sup>6</sup>S. Van den Berghe, F. Miserque, T. Gouder, B. Gaudreau, and M. Verwerft, J. Nucl. Mater. 294, 168 (2001).
- F. Nozaki and K. Ohki, Bull. Chem. Soc. Jpn. 45, 3473 (1972).
- <sup>8</sup>G. Hutchings, C. S. Heneghan, I. D. Hudson, and S. H. Taylor, Nature (London) 384, 341 (1996).
- <sup>9</sup>B. E. Kahn and R. D. Rieke, Chem. Rev. (Washington, D.C.) 88, 733 (1988), and references therein.
- <sup>10</sup>E. M. Carnahan, J. D. Protasiewicz, and S. J. Lippard, Acc. Chem. Res. 26, 90 (1993).
- <sup>11</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865

(1996).

- <sup>12</sup>D. H. Vanderbilt, Phys. Rev. B **41**, 7892 (1990). The ultrasoft pseudopotential of uranium was developed at Ruhr-Universitaet Bochum, Germany, by Dr. Axel Kohlmeyer.
- <sup>13</sup>N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
- <sup>14</sup>J. P. Crocombette, F. Jollet, L. Thien Nga, and T. Petit, Phys. Rev. B 64, 104107 (2002).
- <sup>15</sup>N. Marzari, D. Vanderbilt, A. De Vita, and M. C. Payne, Phys. Rev. Lett. 82, 3296 (1999).
- <sup>16</sup>H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
- <sup>17</sup>PWscf, S. Baroni, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, http:// www.pwscf.org.
- <sup>18</sup>A. K. Ray and J. C. Bouettger, Phys. Rev. B **70**, 085418 (2004).
- <sup>19</sup>G. C. Allen, P. M. Tucker, and J. W. Tyler, J. Phys. Chem. 86, 224 (1982).
- <sup>20</sup>M. N. Hidhili, B. V. Yakshinky, and T. E. Madey, Surf. Sci. 445, 512 (2000).
- <sup>21</sup>S. D. Senanayake, G. Waterhouse, A. S. Y. Chan, D. Mullins, T. E. Madey, and H. Idriss, work conducted at Unit 12 A of the Synchrotron Light Source, Brookhaven National Laboratory November 2004, and in progress. <sup>22</sup>J. C. Boettger and A K. Ray, Int. J. Quantum Chem. **90**, 1470 (2002).
- <sup>23</sup>J. Akella, S. Weir, J. M. Wills, and P. Soederlind, J. Phys.: Condens. Matter 9, L549 (1997).
- <sup>24</sup>X. Wang, Y. Jia, Q. Y. Fei, W. J. Ma, and X. Hu, Surf. Sci. 551, 179 (2004).
- <sup>25</sup>B. D. Sharma, Acta Crystallogr. **16**, 322 (1963).
- <sup>26</sup>Introduction to Surface Chemistry and Catalysis, edited by G. A. Somorjai (Wiley, New York, 1994). <sup>27</sup>E. K. Storms and A. J. Haber, J. Nucl. Mater. **23**, 19 (1967).
- <sup>28</sup>T. Gouder, C. A. Colmenars, J. R. Naegele, J. C. Spirlet, and J. Verbist, Surf. Sci. 264, 354 (1992).
- <sup>29</sup>M. Zhou, L. Andrews, J. Li, and B. E. Bursten, J. Am. Chem. Soc. 121, 9712 (1999).
- <sup>30</sup>J. Li, B. E. Bursten, B. Liang, and L. Andrews, Science 295, 2242 (2002)