Journal of Catalysis **206,** 155–158 (2002)
doi:10.1006/jcat.2001.3483, available online at http://www.idealibrary.com on IDEAL®

Carbon Efficiency and the Surface Chemistry of the Actinides: Direct Formation of Furan from Acetylene over β-UO_3

H. Madhavaram and H. Idriss[1]

Materials Chemistry, Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand

Received September 13, 2001; revised November 27, 2001; accepted November 27, 2001

This work presents the direct oxidative coupling of two molecules of acetylene to furan (C_4H_4O) over the surface of pure polycrystalline β-UO_3. For comparison, only traces of furan are formed over α-U_3O_8 and none on UO_2 surfaces. A comparison to the reactions of other C_2 compounds (ethanol (H. Madhavaram and H. Idriss, *J. Catal.* 184, 553 (1999)), acetaldehyde (H. Madhavaram and H. Idriss, *Catal. Today* 63, 309 (2000)), and ethylene (H. Madhavaram and H. Idriss, *J. Catal.* 184, 553 (1999); H. Madhavaram and H. Idriss, *Stud. Surf. Sci. Catal.* 110, 265 (1997)) over β-UO_3 indicates the presence of two routes for making furan from C_2 compounds: one via aldolization and the other via oxidative coupling. © 2002 Elsevier Science (USA)

Key Words: **uranium oxide; oxidative coupling; actinides; furan.**

INTRODUCTION

The surface chemistry of the uranium oxide system is one of the richest and most complex to investigate. This is due to several factors including the large range of oxidation states and the presence of multiple thermodynamically stable phases; for example, UO_3 exhibits seven polycrystalline structures and one amorphous structure (1). In addition, phase transformation from one structure to another requires very small activation energies making it a real challenge to produce a pure form of the desired phase (probably with the exception of α-U_3O_8).

Consequently, investigating the surface bulk dynamic of these actinide oxides is an essential task. Yet, the surface reaction of pure uranium oxide phases has received very little attention. This work is motivated by the important technological applications of uranium oxide because *it presents* an extension to our basic understanding of the surface reactivity of earlier transition metal oxides and might show new reactions not shared by other oxides; see, for example, H_2 production form water over PuO_2 (2) or the formation of *cis*-endiolates over organometallic compounds of uranium from CO (3). The rich range of stoichiometry and structures might help in designing a system where the dynamic orients toward a desired chemical product. A simple way to view such a surface dynamic is via the "so-called" Mars–van Krevelen mechanism (4), where an adsorbed molecule (such as CO) might be oxidized by lattice oxygen anions to CO_2. As a result the lattice is depleted (due to the formation of oxygen vacancies) and gas-phase oxygen molecules are required to restore these surface point defects. To achieve this, at least two requirements have to be satisfied: (i) high-surface oxygen mobility (oxides containing O^{2-} with a small Madelung potential (5, 6)) and (ii) the presence of surface metal cations having a coordinative unsaturation. For example, Ru^{4+}_{5c} (5c stands for five-fold coordinated) cations of the rutile $RuO_2(110)$ single crystal showed activity for CO oxidation, while Ru^{4+}_{6c} cations (fully coordinated) did not (7). Moreover, the presence of double vacancies may accommodate two adsorbed molecules over one surface cation. This may result in coupling reactions. The Ziegler–Natta polymerization reaction is a chief example (8). The best known example of an oxide surface is the "so-called" ketonization reaction (9, 10) over Ti^{4+}_{4c} of the {114}-faceted $TiO_2(001)$ single crystal in which the dissociative adsorption of carboxylic acids on the cation–anion centers results in carboxylate and hydroxide formation—in general any oxide having one coordinative unsaturation may catalyze this step. However, the presence of two coordinative unsaturations on the Ti^{4+}_{4c} cations is poised to accommodate two carboxylate species that may couple together yielding one molecule of ketone and one molecule CO_2 (11).

This work proves that we succeeded in combining the aforementioned points. In other words, to make furan from acetylene the presence of two coordinative unsaturations and a high-surface oxygen anion mobility is required, and it appears that the surface of β-UO_3 provides this requirement.

Furan and furan derivates, important chemicals in many industrial processes and products such as those in pharmaceuticals, herbicides, stabilizers, and fine chemistry, are commercially manufactured from the decarbonylation of furfural (12–14) and can also be made by oxidation of butadiene (15, 16). All these routes are based on C_4 reactants.

---

[1] To whom correspondence should be addressed. Fax: 64 9 373 7422. E-mail: h.idriss@auckland.ac.nz.

0021-9517/02 $35.00
© 2002 Elsevier Science (USA)
All rights reserved.

Yet, it was recently indicated that it would be challenging to produce furan from these C_4 molecules in a one-step process (17). Moreover, while furan might be a reaction intermediate in the production of maleic anhydride from C_4 hydrocarbons over VPO catalysts (18), a good part of maleic anhydride is converted back to furan! Thus, it is clear, that achieving the direct synthesis of furan from non-oxygen-containing C_2 molecules (such as acetylene) would have a crucial impact on catalysis by oxide materials.

EXPERIMENTAL

β-UO_3 was prepared from a uranium nitrate solution in which $U(OH)_6$ was precipitated with ammonia solution at pH 9. The precipitate was filtered and washed in deionized water, dried at 373 K overnight, and calcined at 773 K for 18 h. Preheating the furnace to 773 K was essential in preventing the formation of the more stable γ-UO_3 and α-U_3O_8 phases. An X-ray diffraction (XRD) spectrum and a scanning electron microscopy image are presented in Fig. 1. Most of the lines in the XRD spectrum can be attributed to the β-UO_3 phase indicating a high purity of the oxide; the relatively high signal-to-noise ratio shows a high crystalline-to-amorphous ratio. Irregularly shaped particles of a size less than 500 nm containing some nanopores (<10 nm) are shown. UO_2 was formed from reduction of α-U_3O_8 by H_2 above 800 K for at least 4 h. X-ray photoelectron spectroscopy (XPS) was previously used to investigate the oxidation states of U cations on the surfaces of UO_2, α-U_3O_8, and UO_3 to quantitatively determine the atomic concentrations of U^{x+} cations on the surface and near surface of these oxides and can be found in Ref. (21). A Spectra Vision quadrupole mass spectrometer (scanning up to 200 amu) connected to a high-vacuum chamber (base pressure ca. 10^{-7} Torr, working pressure during temperature-programmed desorption (TPD) $= 2$–3×10^{-6} Torr) and multiplexed to a PC was used. The ramping rate was kept at $0.25\ \mathrm{Ks}^{-1}$. The cyclic rate was ca. 12 amu/3 s. Thus, spectral resolution was close to 1 K. β-UO_3 powder, 50 mg, was loaded into a fixed-bed quartz reactor and heated to 523 K for 2 h prior to dosing with C_2H_2. Ultrapure C_2H_2 was used at concentration of 10 ppm (Ar balance). The dosing amounts varied from 3.5×10^{-7} to 4.2×10^{-6} mol (per 50 mg). Quantitative reaction products were analyzed following the method described previously (24). The reactor pressure during TPD was ca. 10^{-3} Torr at a pumping speed of ca. 10 m^3/h.

RESULTS AND DISCUSSION

There are two main differences between β-UO_3 and α-U_3O_8: they are structural and electronic. The unit lattice of β-UO_3 is composed of five U^{6+}cations (Fig. 2): three of them are sixfold coordinated to oxygen anions (i.e., containing two coordinative unsaturations, U^{6+}_{6c}) and the remaining two are in a pentagonal bipyramid structure (i.e.,

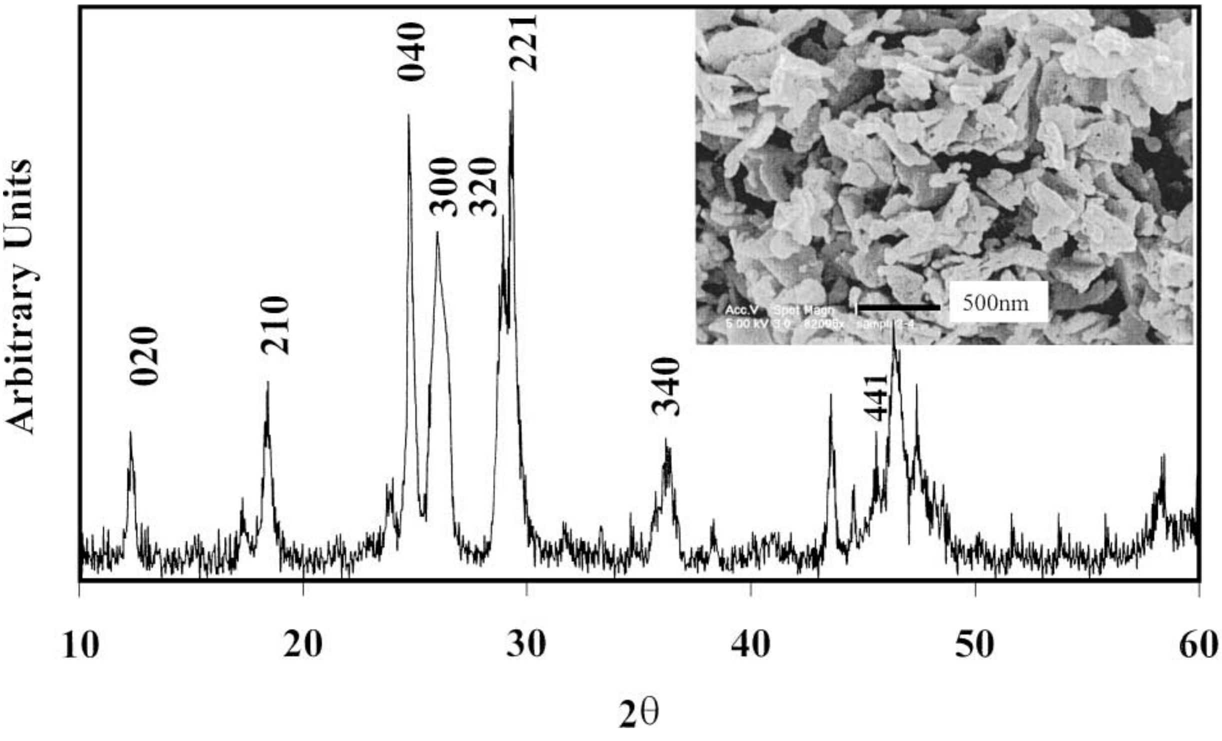


FIG. 1. XRD of pure β-UO_3. An SEM ($E_p = 5$ kV) image of a carbon-coated β-UO_3 sample is inserted. BET surface area = 15 m^2/g.

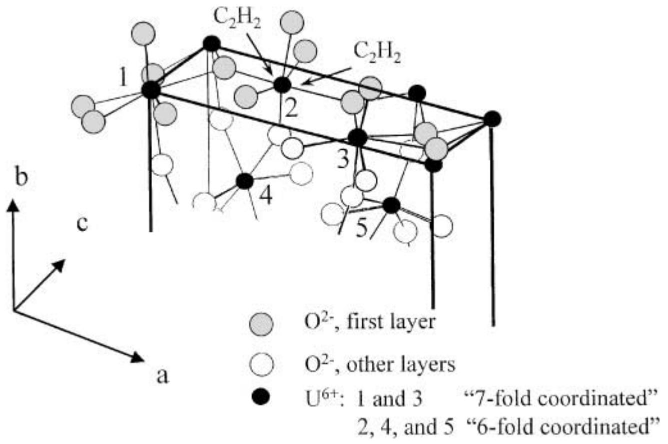


FIG. 2. A schematic representation of the structure of β-UO$_3$. Two molecules of acetylene at the proximity of atom 2 (sixfold coordinated U ion) are also shown. The arrows indicate a plausible adsorption site. The structure is adapted from Ref. (19).

each U cation is sevenfold coordinated to oxygen anions) (19). On the other hand, all U cations of α-U$_3$O$_8$ are sevenfold coordinated to oxygen anions, also in a pentagonal bipyramid structure. While U cations in α-U$_3$O$_8$ are in +6 and +4 oxidation states (in a theoretical ratio of 2 to 1–although we have shown, by detailed analysis of the XPS U4f region that the real surface of U$_3$O$_8$ may be composed of up to 83% of U^{6+} cations (20)), the surface of β-UO$_3$ is composed exclusively of U^{6+} cations (21).

Figure 3 presents TPD of acetylene (total dosing $= 3.5 \times 10^{-7}$ mol) over β-UO$_3$. Three desorption masses are shown: unreacted acetylene (C_2H–, m/e 25), furan molecular weight (C_4H_4O, m/e 68), and furan main fragmentation (C_3H_3, m/e 39). The very low desorption peak temperature at 390 K indicates that the reaction may have been completed during the adsorption process at room temperature. Increasing the dosing amount to 2×10^{-6} and 4.2×10^{-6} mol resulted in the desorption of a small second peak of furan at ca. 450 K. However, the amount of unreacted acetylene remained negligible. These observations might indicate that either the surface is saturated or large amounts of furan are formed at room temperature—while dosing—this formation prevented further adsorption of acetylene molecules. Similar reactions were carried out over α-U$_3$O$_8$, but only traces of furan were observed. These trace amounts are most likely formed over a discrete phase of UO$_3$ at the surface of U$_3$O$_8$ (not observed by XRD). The average furan carbon yield, from four different runs at 3.5×10^{-7} mol/50 mg, was found to be equal to 83% which is equal to ca. 3×10^{-6} mol/g (or 2×10^{-7} mol/m^2; BET surface area ≈ 15 m^2/g of UO$_3$). Catalyst regeneration could be obtained after heating the used oxide in 30 atm of O$_2$ at 673 K for at least 2 h. No other products were observed (with the exception of CO$_2$, mainly formed from bulk transformation of UO$_3$ to U$_3$O$_8$ at $T > 600$ K during TPD).

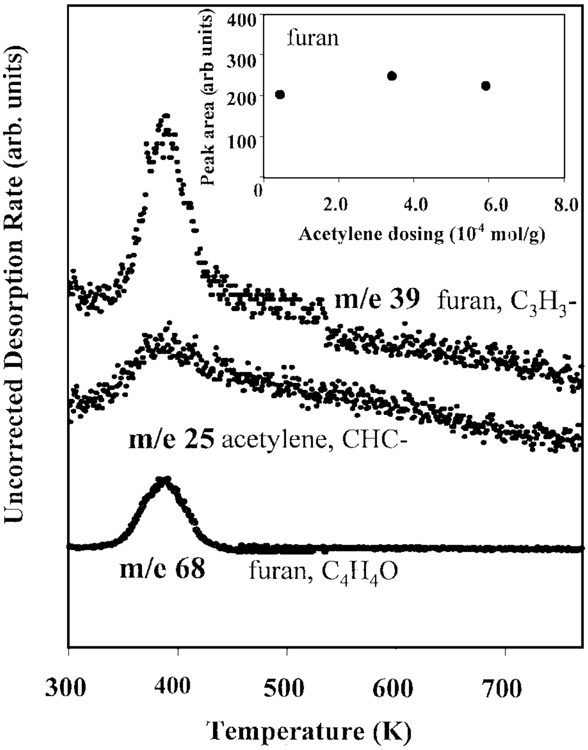


FIG. 3. Temperature-programmed desorption after acetylene adsorption at room temperature over β-UO$_3$. The insert presents the computed furan desorption at a different initial dosing of acetylene. m/e 25 is mainly an acetylene fragment.

We have previously observed the formation of furan from ethanol (20), acetaldehyde (22), and ethylene (20, 23). Although the highest yield for furan (prior to this work) was observed from acetaldehyde, considerable formation of crotonaldehyde (formed by β-aldolization of two molecules of acetaldehyde) was also observed. (Furan is easily formed from crotonaldehyde.) Moreover, acetaldehyde was formed from ethylene as well as from ethanol

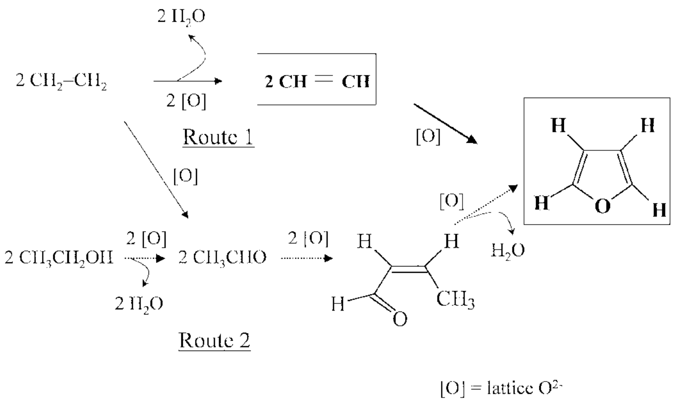
TABLE 1

Carbon Selectivity of Furan during TPD of Four Different C$_2$ Molecules over β-UO$_3$[a]

Reactant	Furan selectivity (C%)	Other products	TPD, peak temperature (K)	References
$CH_2{=}CH_2$	5–6	CH_3CH_2OH CH_3CHO	510	23
CH_3CH_2OH	20–25	CH_3CHO	510	20
CH_3CHO	30–40[b]	C_4H_6O,[b] crotonaldehyde	420	22
CHCH	≈100	—	390	This work

[a] The activity to furan is in the following order: $CH_2CH_2 < CH_3CH_2OH < CH_3CHO <$ CHCH.

[b] Selectivity changed with coverage.



SCHEME 1. Two distinct routes for making furan from C_2 compounds over β-UO_3. Route 1. Coupling of two molecules of ethylene (or two molecules of acetylene) followed by oxidation to furan. Route 2. Aldolization of acetaldehyde, followed by C–O bond formation (and cyclization).

adding a further complication to the scheme. The absence of acetaldehyde and crotonaldehyde, during acetylene-TPD, clearly suggests the presence of a direct route for making furan from acetylene.

Table 1 compares data for furan formation from the four different C_2 molecules, while Scheme 1 shows the two routes as evidenced from TPD studies.

CONCLUSION

Uranium oxide is considered to be a very good catalyst for *oxidation* reactions (25, 26), and bare U atoms are very active for *carbon–carbon coupling* reactions (27). This work demonstrates that both routes can be successfully combined on β-UO_3 as evidenced by the direct synthesis of furan (C_4H_4O) from acetylene (C_2H_2).

REFERENCES

1. Colmenares, C. A., *Prog. Solid State Chem.* **15**, 257 (1984).
2. Haschke, J. M., Allen, T. H., and Morales, L. A., *Science* **287**, 285 (2000).
3. Kahn, B. E., and Rieke, E. D., *Chem. Rev.* **88**, 733 (1988).
4. Mars, P., and van Krevelen, D. W., *Chem. Eng. Sci.* **3**, 41 (1954).
5. Idriss, H., and Barteau, M. A., *Adv. Catal.* **45**, 261 (2000).
6. Chong, S. V., Griffiths, T. R., and Idriss, H., *Surf. Sci.* **444**, 187 (2000).
7. Over, H., Kim, Y. D., Seitsonen, A. P., Wendt, S., Lundgren, E., Schmid, M., Varga, P., Morgante, A., and Ertl, G., *Science* **287**, 1474 (2000).
8. Boor, J., Jr., "Ziegler–Natta Catalysts and Polymerizations." Academic Press, New York, 1979.
9. Kim, K. S., and Barteau, M. A., *J. Catal.* **125**, 353 (1990).
10. Idriss, H., Kim, K. S., and Barteau, M. A., *Stud. Surf. Sci. Catal.* **64**, 327 (1991).
11. Barteau, M. A., *Chem. Rev.* **96**, 1413 (1996).
12. Othmer, K., "Ecyclopedia of Chemical Technology," third edition, Vol. 11. Wiley, New York, 1982.
13. Banford, W. H., and Manes, M. M., U.S. Patent 2 846 449, 1958.
14. Manly, D. G., U.S. Patent 3 021 342, 1962.
15. Garnett, D. I., and Peterson, M. L., U.S. Patent 4 172 838, 1978.
16. Farha, F. E., Jr., U.S. Patent 3 906 009, 1975.
17. Wilderberg, M. D., Mallat, T., Gobel, U., and Baiker, A., *Appl. Catal. A* **68**, 69 (1998).
18. Taufiqyaq, Y. H., Sakakini, B. H., and Waugh, K. C., *Catal. Lett.* **46**, 273 (1997).
19. Debets, P. C., *Acta Crystallogr.* **21**, 589 (1966).
20. Madhavaram, H., and Idriss, H., *J. Catal.* **184**, 553 (1999).
21. Madhavaram, H., Buchanan, P., and Idriss, H., *J. Vac. Sci. Technol. A* **15**, 1685 (1997).
22. Madhavaram, H., and Idriss, H., *Catal. Today* **63**, 309 (2000).
23. Madhavaram, H., and Idriss, H., *Stud. Surf. Sci. Catal.* **110**, 265 (1997).
24. Idriss, H., Kim, K. S., and Barteau, M. A., *J. Catal.* **139**, 119 (1993).
25. Hutchings, G. J., Heneghan, C. S., Hudson, I. D., and Taylor, S. H., *Nature* **384**, 341 (1996).
26. Nozaki, F., and Ohki, K., *Bull. Chem. Soc. Jpn.* **45**, 3473 (1972).
27. Heinemann, C., Cornehl, H. H., and Schwartz, H., *J. Organomet. Chem.* **501**, 201 (1995).