Inorganica Chimica Acta, 140 (1987) 37–38

Surface Studies of UFe_2 and Evaluation of its Catalytic Properties with a $2H_2$:CO Mixture[*]

J. SCHULTZ, C. A. COLMENARES[†]

University of California, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, Calif. 94550, U.S.A.

J. NAEGELE and J. C. SPIRLET

Commission of the European Communities, European Institute for Transuranium Elements, Postfach 2340, D-7500 Karlsruhe, F.R.G.

As part of a long-term program to study the catalytic properties of actinides and their intermetallic compounds, we have investigated the high-pressure reaction of H_2 and CO to form hydrocarbons over crushed UFe_2 and the complimentary reactions of O_2, CO and CO_2 with the surface of polycrystalline UFe_2, studied under ultra-high vacuum conditions.

Experimental

The surface reactions were followed by X-ray photoelectron spectroscopy (XPS) using Al Kα radiation and a double pass CMA (FWHM Au $4f_{7/2}$ = 2.0 eV). Sample cleaning was performed by argon ion (2–3 kV) bombardment, which is expected to result in a slight depletion of Fe from the surface.

The high-pressure reactions were carried out in a copper-lined, differential flow reactor and the products analysed by gas chromatography. A $2H_2$:1CO mixture at 50 atm was passed over 3.5 g of finely ground UFe_2.

Results and Discussion

The surface composition of an initially sputtered-clean surface of UFe_2, as a function of O_2 exposure, is shown in Fig. 1. Atomic concentrations were calculated using empirically derived sensitivity factors for the U 4f, Fe 2p and O 1s core level peaks [1], thus the resulting concentrations may only be accurate to 25% although relative concentration changes are much more reliable. For a sputtered-clean UFe_2 surface the binding energies of the U $4f_{7/2}$ and Fe $2p_{3/2}$ core levels are 377.8 and 707.1 eV, respectively, and the Fe/U ratio is $\simeq$2.0. Progressively more of the uranium is oxidized to UO_2 for exposures from 5 to 80 L O_2 (L = Langmuir). This assignment is made on the basis of new U 4f peaks which contain an increasingly larger fraction of the total U 4f intensity as a function of exposure. The U $4f_{7/2}$ peak for UO_2 appears at 380.2 eV and its distinctive shakeup satellite is 6.7 eV from the U $4f_{5/2}$ peak [2]. After a 80 L O_2 exposure, the uranium in the surface region analysed ($\simeq$50 Å) is completely oxidized. The Fe 2p spectrum shows no significant change up to this level of oxygen exposure, indicating that the iron remains metallic. The Fe/U ratio decreases dramatically with exposures from 5 to .80 L O_2 (Fig. 1) suggesting that uranium is segregating to the surface, driven by UO_2 formation.

Iron oxidation occurs with oxygen exposure from 160 L to 1280 L O_2, as indicated by an increasing

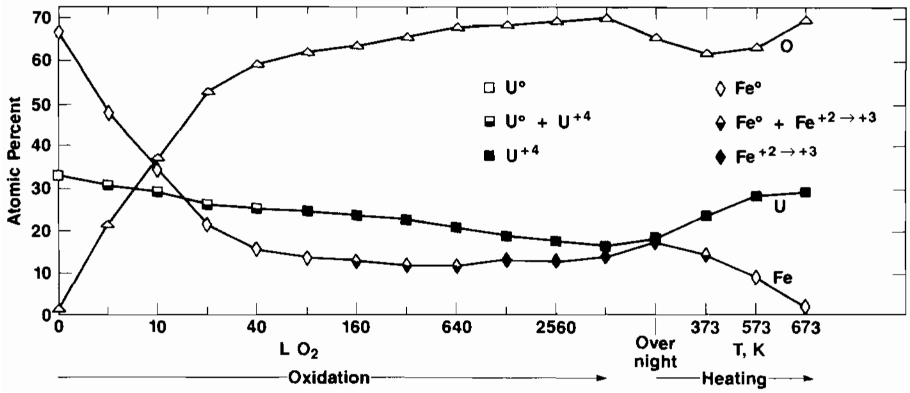

Fig. 1. Atomic percent obtained from XPS of initially sputtered-clean UFe_2 surface after exposure to O_2 and then annealing. Oxidation states of U and Fe are indicated.

---

[*] Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48. Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

[†] Author to whom correspondence should be addressed.

0020-1693/87/$3.50

fraction of the Fe $2p_{3/2}$ and $2p_{1/2}$ peak intensities appearing ≃3 eV higher than their metallic positions. There is a slight increase in the Fe/U ratio accompanying the iron oxidation (Fig. 1), suggesting a partial reversal of the segregation of uranium to the surface observed at lower oxygen exposures. From 1280 L to 5120 L O_2, the binding energy of the Fe $2p_{3/2}$ peak is 710.4 eV, which falls between the values determined for Fe^{2+} and Fe^{3+} species in pure iron oxides, 709.7 and 711.2 eV [3], respectively. However, the Fe $2p_{3/2}$ peak shape does not appear to indicate the presence of both species. The poor match of our results with the binding energies observed for pure iron oxides may reflect the formation of a $U_xFe_yO_z$ mixed oxide.

Annealing this highly oxidized sample up to 673 K, followed by cooling to ≃323 K to take photoelectron spectra, reduces the iron to its metallic state and produces a dramatic decrease in the Fe/U ratio (Fig. 1), resulting from additional UO_2 segregation to the surface. Also, the U 4f, U 4d, O 1s and U 5f peaks shift to higher binding energies by 0.7 eV. An explanation for this observation is that annealing causes an upward shift of the Fermi level within the band gap of uranium oxide.

The reactions of CO and CO_2 with the sputtered-clean UFe_2 surface are very similar to each other and distinctly different from that of O_2 in that they saturate at about 20 L gas exposure. These reactions cause some segregation of uranium to the surface (Fe/U ≃ 1.7). 20 L of either CO or CO_2 results in an O 1s peak at 530.4 or 530.2 eV, respectively, very close to the O 1s peak at 530.4 eV after 20 L O_2. Binding energies of 282.7 or 282.6 eV for the C 1s core level after CO or CO_2 exposure, respectively, are very close to values observed for atomic C on other metals [4]. A broadening of the U 4f peaks, but no change in the Fe 2p spectrum, is observed compared to the spectrum of the clean surface. Thus the spectra indicate that CO and CO_2 dissociate on the sputtered-clean surface of UFe_2 and that the oxygen reacts with uranium to form uranium oxide. Using empirically derived sensitivity factors [1], the O/C ratios calculated after saturation with CO and CO_2 are 2.0 and 3.6, respectively. These are larger than the stoichiometry of the reacting gases. Also, the O/C ratio is about two times larger in spectra taken from a grazing angle (≃10°), where the surface sensitivity of the technique is further enhanced, than in spectra taken from a normal angle of incidence. These observations are consistent with the oxygen atoms being on the surface of the solid and the carbon atoms being deeper into the analysed layer.

UFe_2 ground into a fine powder was tested as a catalyst with a $2H_2$:1CO mixture under the same conditions used to produce methanol over ThO_2 [5]. Preliminary results show that UFe_2 produces a significant amount of methanol (61.8 weight % of the products) at 577 K, but that hydrocarbons are the main products at 739 K. The product distribution in weight % is: 25.4 methane, 4.2 ethylene, 6.4 ethane, 23.6 propane, 21.8 i-butane, 4.0 n-butane, 5.4 i-pentane, 3.8 n-pentane, 5.4 n-heptane, and <0.2 methanol. The 25.4 weight % methane of the products represents 0.14 weight % in the effluent gas. Four unidentified products with more than eight carbons are also detected. The hydrocarbon products at both temperatures follow the product distribution predicted by the Schulz–Flory polymerization model. Raising the reactor to 783 K after 108 h at 577 K causes severe coking of the catalyst. XPS analysis of the used catalyst indicates that uranium is present as UO_{2+x} and iron as Fe_2O_3, with a Fe/U ratio of 1.2.

References

1 C. D. Wagner, L. E. Davis, M. V. Zeller, J. A. Taylor, R. H. Raymond and L. H. Gale, *Surf. Interface Anal.*, *3*, 211 (1981).

2 G. C. Allen, P. M. Tucker and J. W. Tyler, *J. Phys. Chem.*, *86*, 224 (1982).

3 C. R. Brundle, T. J. Chuang and K. Wandelt, *Surf. Sci.*, *68*, 459 (1977).

4 C. R. Brundle, *IBM J. Res. Develop.*, *22*, 235 (1978).

5 J. Maj, C. A. Colmenares and G. A. Somorjai, *J. Catal.*, *95*, 385 (1985).