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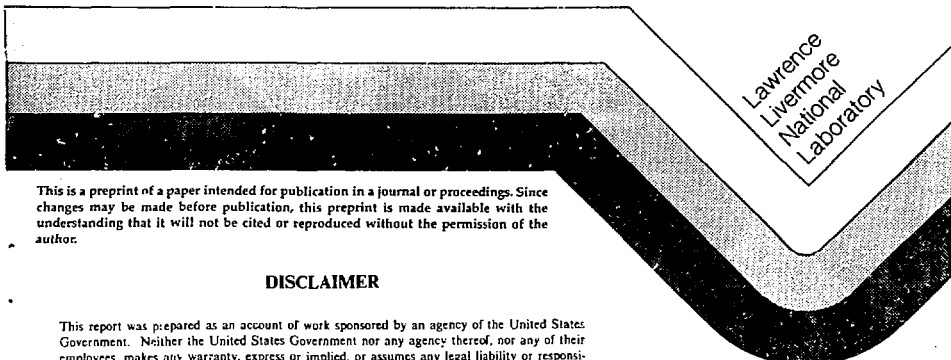
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of its Catalytic Properties
With a $2H_2:CO$ Mixture

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

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Abstract

The reactivity of UFe_2 with O_2 , CO and CO_2 were studied using x-ray photoelectron spectroscopy (XPS). Adsorption of O_2 on clean UFe_2 surfaces ($Fe/U=2.0$), produced by argon-ion sputtering, leads to the formation of UO_2 and depletion of Fe from the surface layer probed by XPS ($Fe/U=0.8$). The oxidation state of Fe in this layer, as determined by XPS ($Fe\ 2p_{3/2} = 710.4\ eV$), is between Fe^{+2} and Fe^{+3} of pure Fe oxides. Exposure of sputtered-clean UFe_2 to CO and CO_2 results in a slight broadening of the U 4f peaks indicating U oxidation, and some Fe depletion in the analyzed layer ($Fe/U=1.7$). The O 1s (530.2 and 530.4 eV for CO and CO_2 , respectively) and C 1s (282.7 and 282.6 eV for CO and CO_2 , respectively) indicate that dissociative chemisorption to O and C atoms occurs.

UFe_2 ground into a fine powder was tested as a catalyst in a differential high-pressure flow reactor with a $2H_2:CO$ gas mixture. A significant amount of methanol and hydrocarbons are produced at 577K; while hydrocarbons are the main products (>99%) at 739K. XPS analysis of the used catalyst indicates that U is present as UO_{2+x} and Fe as Fe_2O_3 .

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Introduction

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 $K\alpha$ radiation and a double pass CMA (FWHM Au $4f_{7/2} = 2.0$ eV). Sample cleaning was performed by argon ion (2-3kV) 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 analyzed by gas chromatography. A $2H_2:1CO$ mixture at 50 atmospheres was passed over 3.5g 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 Figure 1. Atomic concentrations are 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 ≈ 2.0 . Progressively more of the uranium is oxidized to UO_2 for exposures from 5 to 80L O_2 . 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 80L O_2 exposure, the uranium in the surface region analyzed ($\approx 50\text{\AA}$) 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 80L O_2 (Fig. 1) suggesting that uranium is segregating to the surface, driven by UO_2 formation.

Iron oxidation occurs with oxygen exposure from 160L to 1280L O_2 as indicated by an increasing 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 1280L to 5120L 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 673K, 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 4i, 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 UF_6 surface are very similar to each other and distinctly different from that of O_2 in that they saturate at about 20L gas exposure. These reactions cause some segregation of uranium to the surface ($Fe/U \approx 1.7$). 20L 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 20L 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 UF_6 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 ($\approx 10^\circ$), 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 analyzed layer.

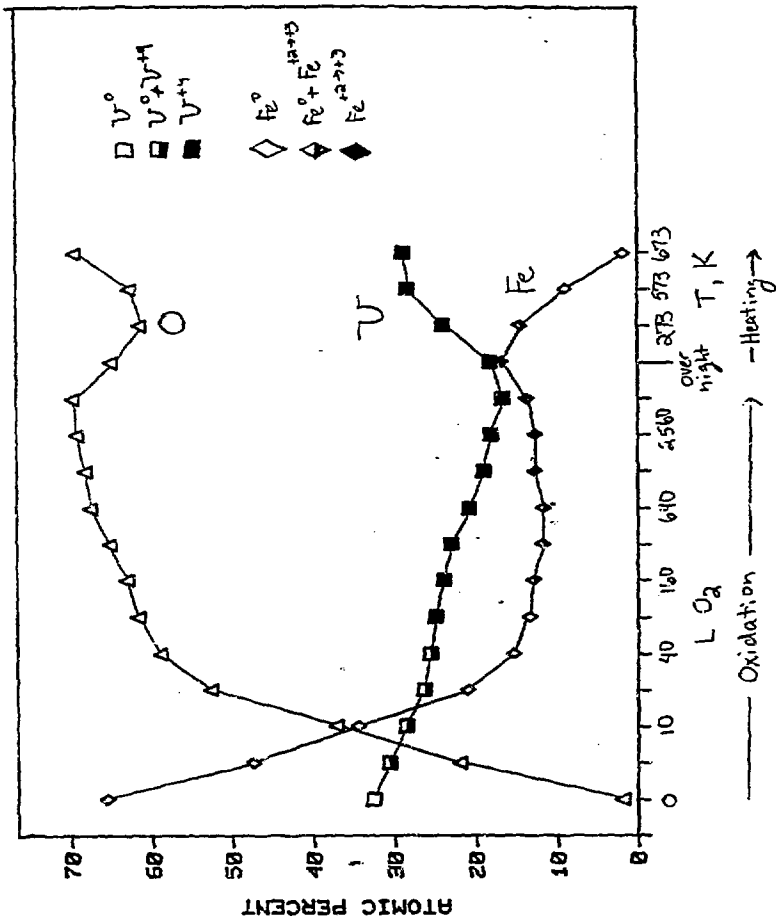
UFe₂ was tested as a catalyst with a 2H₂:1CO mixture under the same conditions used to produce methanol over ThO₂ [5]. Preliminary results show that UFe₂ produces a significant amount of methanol (61.8 weight % of the products) at 577K, but that hydrocarbons are the main products at 739K. The product distribution in wt % 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 wt % methane of the products represents 0.14 wt % 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 783K after 108 hours at 577K causes severe coking of the catalyst. XPS analysis of the used catalyst indicates that uranium is present as UO_{2+x} and iron as Fe₂O₃, 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).

Figure 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.



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