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CRTA STUDY OF THE REDUCTION OF UO_2F_2 INTO UO_2 BY DRY H_2

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Abstract

The reduction of UO_2F_2 by dry H_2 was studied by Controlled Rate EGA, with a special set-up operating under a gas flow under atmospheric pressure. At the constant transformation rate seected, this reduction apparently takes place in one main step, around 450°C (for a total duration of 100 h), followed by a small exothermic step. The final product is a stoichiometric, well crystallized UO_2. XRD analysis shows the occurrence of two successive intermediates of which one has a structure close to that of UO_2, but with interstitial fluorine atoms.

Keywords: CRTA, Sample Controlled Thermal Analysis, Temperature Programmed Reduction, UO_2, UO_2F_2

Introduction

This study was carried out in the scope of ^{235}U enrichment by the diffusion process which makes use of uranium hexafluoride UF_6 as the diffusing species. After this step, ^{235}U must be recovered in the form of uranium dioxide UO_2 suitable for making the pellets of nuclear fuel used in the plants. This transformation into UO_2 can be carried out through a dry process: UF_6 is first hydrolysed into uranium oxyfluoride UO_2F_2, which is then reduced, by dihydrogen in the presence of water vapour, into UO_2 [1].

It is principally the role of water vapour in the latter reaction which we aimed to elucidate. For this purpose, we decided to split the study in two parts: one dealing with the influence of water vapour on the porous structure of UO_2F_2 and the other – which is the main subject of this paper – dealing with the reduction of UO_2F_2 by dihydrogen in the absence of water vapour. Here, we directly considered the influence, on the course of the reaction and on the intermediate compounds, of the porous structure of the starting UO_2F_2.

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Experimentals

In this study, in view of limiting at will the pressure and temperature gradients which can heavily complicate the interpretation, we decided to make use of Controlled Transformation Rate EGA [2] in order to be able to control the reaction at very low rates (reaction durations above 48 h).

A CR-EGA apparatus operating under a gas flow at atmospheric pressure was specially designed and built for this purpose [3]. It is based on the use of a high-sensitivity, differential, gas flowmeter (there is a sample side and a reference side with similar design) which is a kind of pneumatical equivalent of the electrical Wheatstone bridge. Here, indeed, the four electrical resistors are replaced by constrictions (i.e. pneumatical resistors) whereas the detection of a voltage drop (by a voltmeter) is replaced by the detection of a pressure drop (by a differential pressure gauge). Any difference in gas flow between the two arms of the bridge (due to either consumption or evolution of gas on the sample side) gives rise to a signal provided by the pressure gauge and used to control the heating of the sample. The sensitivity of this set-up is such that it allows to keep at a constant rate a reaction producing no more than a few cm^3 STP of gas per hour.

This set-up is suited for the study of any thermal reaction involving gas (G) and solid (S) phases:

$$aS_1 + bG_1 = cS_2 + dG_2$$

provided the gas evolution does not exactly balance the gas consumption (b≠d).

An interesting feature of CRTA is that, when slow rates of reaction are selected, the sample can easily be quenched, at any time of the reaction, in a highly reproducible and meaningful state which can be considered to be exactly on the path of the reaction. It can then be studied, subsequently, by other techniques, specially XRD.

Results and discussion

CRTA

We give in Fig. 1 the CRTA curve recorded during the reduction, by pure, dry H_2, of a hydrated sample of uranyl fluoride ($UO_2F_2{\cdot}2.8H_2O$). Two steps are clearly seen. The first one, around 90°C, corresponds to dehydration, whereas the second one, around 450°C, is due to the reduction proper. The latter step ends with a small but visible (and reproducible) 'valley'. Such a temperature depression (which, by principle, never occurs in conventional thermal analysis) can occur in CRTA experiments and reveals a change in the reaction mechanism (a lower temperature is sufficient to keep the reaction rate at the same level). This is to be connected to an observation by Favre [4] that, at the end of the reduction of UO_2F_2 by dry H_2, DTA shows the occurrence of a 'very narrow and important' exothermal peak. He also noticed an increase of the rate of reaction close to its completion. Favre thought of the existence of an intermediate product prior to UO_2, but could not evidence it neither by chemical analysis nor by XRD.

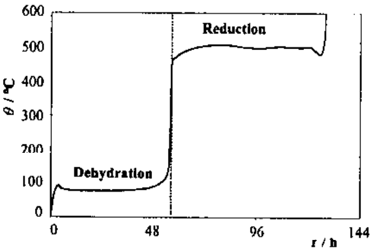

Fig. 1 Controlled Rate transformation Thermal Analysis (CRTA) of the reduction of $UO_2F_2 \cdot 2.8H_2O$ by dry H_2

Although approximately isothermal, the reduction step actually shows small, reproducible fluctuations which could be explained by the occurrence of several simultaneous and/or successive reactions.

We started from three samples with different initial BET (N_2) specific surface area (9.7 to 19.7 $m^2 g^{-1}$) but did not see any difference in the reduction step. This can be due to the fact that, at the temperature where the reduction takes place, the specific surface areas of the three samples have already dropped down to a common value: we have checked that a heating at 400°C was enough to produce a partial sintering of UO_2F_2 by coalescence of the crystallites, as seen by XRD. Let us also notice that the partial pressure of H_2 could be changed from 1 to 0.5 bar (the complementary carrier gas then being nitrogen) without influencing the CRTA curve.

XRD

We report in Fig. 2 a succession of 9 XRD patterns recorded at various stages of the reduction step. The bottom pattern is that of the pale yellow sample of anhydrous UO_2F_2, just after being heated up to 400°C and prior to any reduction (α=0). During the first third of the reduction (i.e. for the next 3 patterns) the sample becomes clear grey. The diffraction peaks of UO_2F_2 diminish to the benefit of a new set of peaks. The X-ray diffraction pattern of this compound resembles that of α-U_3O_8; however several differencies in the angular positions of the peaks allow us to distinguish this

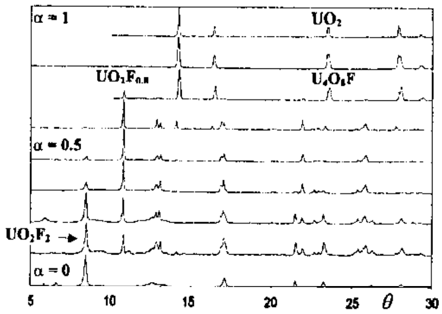

Fig. 2 XRD patterns of the successive compounds isolated during the reduction of $UO_2F_{0.8}$ by dry H_2

new phase whose composition $UO_2F_{0.8}$ was determined during a complementary TG study [5]. As the reduction proceeds, the sample turns deep grey. Although UO_2F_2 is still present in small amount, a new set of peaks develops and can be attributed to a new phase very close to UO_2. It is only at the very end of the reduction, during the small temperature depression observed in the CRTA curve, that the sample becomes clear brown, whereas the only visible peaks are those of UO_2 and of the new phase. The latter peaks are located at slightly larger angles than those for pure UO_2 and they progressively shift to those of UO_2 as the reaction approaches completion. This observation brings us to the conclusion that this new phase simply accomodates interstitial fluorine in an UO_2 network.

Conclusions

The combined use of Controlled Rate EGA (with a special set-up operating under atmospheric pressure) and of XRD therefore shows the occurrence of three successive (but also in part simultaneous) steps in the reduction of UO_2F_2 by dry H_2, all of them involving fluorinated intermediates :

(1) $UO_2F_{2(s)} + 0.6H_{2(g)} = UO_2F_{0.8(s)} + 1.2HF_{(g)}$
(2) $4UO_2F_{0.8(s)} + 1.1H_{2(g)} = U_4O_8F_{(s)} + 2.2HF_{(g)}$
(3) $U_4O_8F_{(s)} + 0.5H_{2(g)} = 4UO_{2(s)} + HF_{(g)}$

It may also be worthwhile noting that the final UO_2 obtained by dry reduction of UO_2F_2 in our experimental conditions is:

- stoichiometric
- well crystallized
- with a BET (N_2) specific surface area of 1.2 m^2g^{-1}
- with particles of 0.2 μm diameter (from XRD)
- with an absolute density (from water pycnometry) of 10.4 $cm^3 g^{-1}$ (to be compared with the theoretical density 10.96 $cm^3 g^{-1}$).

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