In situ infrared spectroscopic study of uranium oxides during UO3 carboreduction

Florence Poncet, Françoise Valdivieso, Raymonde Gibert, Michèle Pijolat

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F. PONCET, F. VALDIVIESO, R. GIBERT and M. PIJOLAT

Centre SPIN, Ecole des Mines, 158 cours Fauriel

42023 Saint-Etienne, Cedex 2 FRANCE.

Abstract :

Carboreduction of UO_3 has been studied by in situ infrared spectroscopy in order to detect the presence of carbon monoxide during the reduction. From thermogravimetry, the reaction was observed to occur in two steps : (i) reduction of UO_3 to U_3O_8 by carbon at 440°C and (ii) reduction at 590°C of U_3O_8 to UO_2 by carbon. No carbon monoxide was observed during the reaction. Nevertheless, formation of carboxylate species are observed at temperature below 550°C with absorption bands at 1017 and 1300 cm^{-1}.

1- Introduction

Reduction of uranium trioxide by carbon was carried out in order to obtain uranium dioxide, intermediate currently used for the preparation of nuclear combustible.

According to the literature [1], the carboreduction of UO_3 to UO_2 is proceeds in two stages (1) the conversion of UO_3 to U_3O_8 and (2) the reduction of U_3O_8 to UO_2 by reaction with carbon. Nevertheless, the mechanism of reduction of U_3O_8 to UO_2 still controversy. In fact, some authors like Lawrance and O'Connor [2] reported that during the reduction, a mixture of carbon monoxide and carbon dioxide is evolved. So, for some authors [3] a fraction of the carbon monoxide contribute to the reduction of U_3O_8. Whereas for Mukerjee et al. [4], which found only carbon dioxide in the gas product, the reduction is only due to the carbon.

To elucidate this difference and in order to better know the reactionnal intermediates during the carboreduction, we have performed the reduction of UO_3 by thermogravimetric analysis (TGA) and in situ infrared spectroscopy.

Our aim was to look for the presence or not of carbon monoxide at the uranium oxide surface during the transformation. According to the literature [5], adsorption of carbon monoxide on oxides produces absorption bands in the region of 2100 - 2000 cm^{-1}.

2 - Experimental results

2-1 Thermogravimetric analysis

Thermogravimetric study was performed in a SETARAM TAG 24 thermobalance equipped with a BALZERS mass spectrometer for the analysis of the evolved gases. The sample used was a powder resulting from the mixture with a slight manual grinding of β-phase uranium trioxide with an excess of carbon (in a

C/U = 3 mole ratio). The sample size in each experiment is 28 mg. The reaction occurs under two liters per hour of flowing helium with a 5°C/min heating rate up to 900°C.

Figure 1 show the results of the thermogravimetric analysis and figure 2 gives the analysis of the evolved gas during heating.
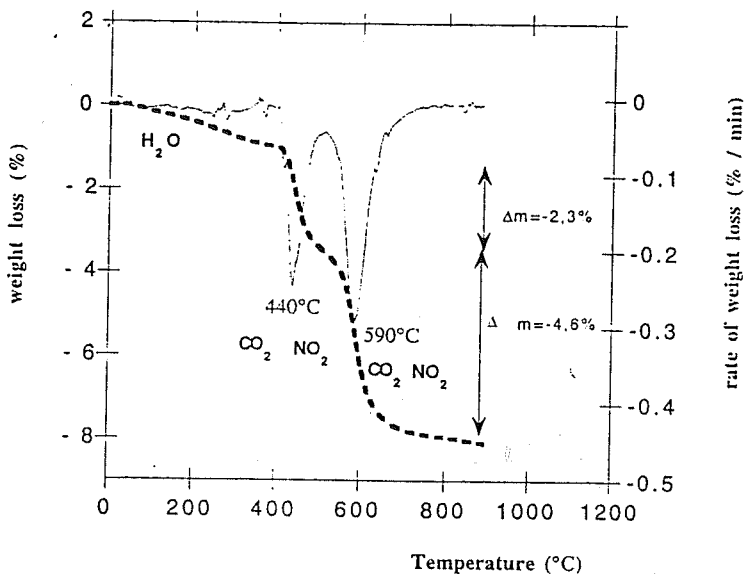

Figure 1 : Curves of weight loss (%) and rate of weight loss (%:min) versus temperature (°C)
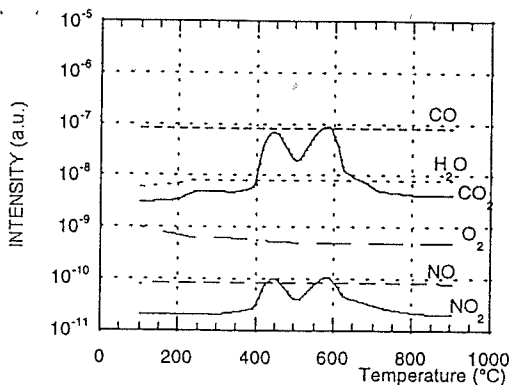

Figure 2 : Gas evolving followed by mass spectrometer during heating, arbitrary unit versus temperature (°C)

We can notice principally on the figure 1 two successive steps in weight loss, whose the maximun rates occur at 440 and 590°C. These weight losses, respectively 2.3 and 4.6 % are accompanied by emission of nitrogen dioxide and essentially carbon dioxide (figure 2). The nitrogen dioxide is two order magnitude less in intensity than carbon dioxide. So, the nitrogen dioxide does not contribute to the weight loss. A small weight loss, inferior to 1%, is appearing between room temperature and 200°C, is only due to the desorption of water.

The weight loss observed at 440°C (2.3%), is equivalente to the theoretical weight loss calculated for the reduction of UO_3 to U_3O_8 by carbon from the initial mass of the mixture, according to (1) :

$$3 \, UO_3 + \tfrac{1}{2} \, C \rightarrow U_3O_8 + \tfrac{1}{2} \, CO_2 \qquad (1)$$
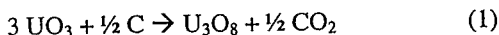
The weight loss observed at 590°C (4.6%) is due to the reduction by carbon of the intermediate oxide U_3O_8 to UO_2 (theoretical value calculated from initial mass of mixture is 4.66%), according to (2) :

$$U_3O_8 + C \rightarrow 3UO_2 + CO_2 \qquad (2)$$
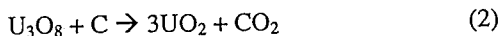
A complementary analysis by X-ray diffraction of the samples obtained at an intermediate step (450°C) and at the end of the heating (900°C) confirms the formation of the compound U_3O_8 and the uranium dioxide, respectively.

2-2 In-situ infrared analysis

The results of in situ infrared analysis are given in figures 3, 4 and 5. In situ infrared spectra have been carried out under flowing argon by means of a FTIR Bio-Rad spectrometer equipped with a high temperature environmental chamber (HTEC) model 0030-103 of Spectra Tech.

The infrared spectra are obtained using diffuse reflectance. A complete scan from 4000 to 400 cm^{-1} is given in transmittance in figures 3 and 4. The maximum transmittance is observed between 1000 to 400 cm^{-1}, so a detailed scan in Kubelka-Munk is shown figure 5 in this region.
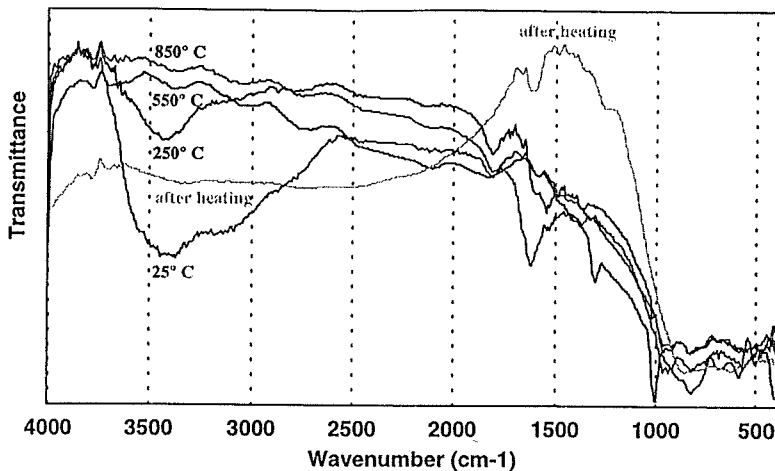
Figure 3: In situ FTIR spectra of UO_3 and C mixture under argon in range of 4000 to 400 cm^{-1} at various temperatures

At room temperature and until 350°C (figure 3), the infrared spectra show absorption bands at 1640 and above 3000 cm^{-1}. These bands disappear during heating, they are due to the presence of adsorbed water and are assigned respectively to the bending and stretching symmetric and asymmetric vibrations of H_2O molecule.
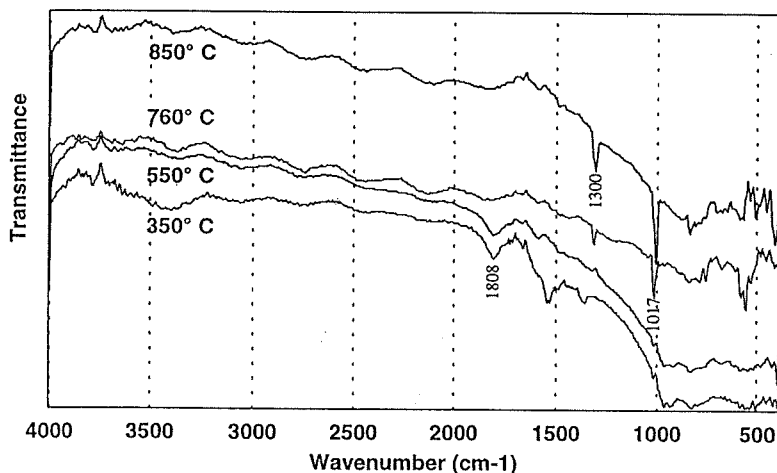

Figure 4: In situ FTIR spectra of UO_3 and C mixture under argon in range of 4000 to 400 cm^{-1} at various temperatures

The figure 4 shows also a band at 1800 cm⁻¹ between room temperature and 550°C. This band is accompanied by bands in the region of 900 cm⁻¹. When the temperature raised up 550°C, the spectra change drastically with disappearance of the bands at 1800 and 900 cm⁻¹ to give bands at 1300 and 1017 cm⁻¹ and a slight shift in lower wavenumber of the bands at 900 cm⁻¹. After cooling the sample at room temperature (figure 3), the bands at 1300 and 1017 cm⁻¹ disappear.

In order to understand the behavior of our solid during heating, we have represented figure 5 the infrared spectra results in the region of the solid frequencies vibration (1000 to 400 cm⁻¹) in Kubelka-Munk.
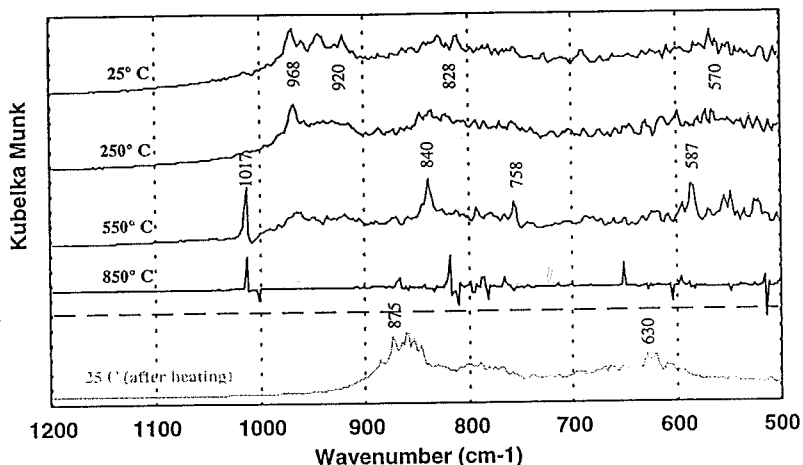

Figure 5 : In situ FTIR spectra of UO_3 and C mixture under argon
in range of 1200 to 500 cm⁻¹ at various temperatures

At room temperature and until 350°C (figure 5), the absorption bands observed at 570 - 828 - 920 and 968 cm⁻¹ are assigned to the absorption bands of β-UO_3, according to the literature [6-8]. From 450°C to 760°C, infrared spectra change with a decrease in absorption bands at 968 and 920 cm⁻¹ and the appearance of an absorption band at 758 cm⁻¹. This band is assigned to the U-O streching vibration of the uranium octoxide U_3O_8. At 850°C and after cooling a broad absorption band is observed around 875 cm⁻¹ which was interpreted by Colmenares [9] as an optical phonon frequency of UO_2 phase.

3 - Discussion and conclusion

Consequently, carboreduction of UO_3 occurs in two steps : (1) reduction of uranium trioxide in uranium octoxide at 440°C by carbon and (2) reduction at 590°C of U_3O_8 in uranium dioxide by carbon. The main gas observed during carboreduction is carbon dioxide. We can note (figure 2) the end of carbon dioxide

emission around 700°C, the carboreduction of U_3O_8 in uranium dioxide is probably finished at this temperature.

During in situ infrared analysis we have reduced the UO_3 in UO_2 via U_3O_8 at the same temperature range as thermogravimetric analysis. But, no absorption band is observed in the region of 2000-2200 cm^{-1}, we can see only an absorption band at 1880 cm^{-1} between 25 to 550°C, this band is assigned to the harmonic of the absorption band at 920 cm^{-1}. Consequently, carbon monoxide was not observed which is in agreement with the reactions (1) and (2).

However the presence of the bands at 1017 and 1300 cm^{-1} at temperature below 550°C is probably due to the chemisorbed carboxylate on the uranium oxyde surface. According to the litterature [5], carboxylate adsorbed on oxides (CO_3^-) display absorption bands in the region : 1090-1020 cm^{-1} and 1450-1420 cm^{-1}. The formation of carboxylate may be explained by the presence of gaseous carbon dioxide observed previously by thermogravimetry during the carboreduction.

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