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Reduction of uranium oxide U_3O_8 into uranium dioxide UO_2 by ammonia

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Key words:

uranium oxide ; reduction ; ammonia ; decomposition ; hydrogen

Abstract

The reduction of uranium oxide U_3O_8 into uranium dioxide UO_2 has been studied by temperature programmed thermogravimetry, up to 700°C. Experiments have been carried out either in ammonia (P_{NH3} ranging from 35 to 125hPa) or hydrogen (P_{H2} ranging from 42 to 243hPa). The gases evolved and consumed during the reduction were followed simultaneously by mass spectrometry. The reduction of U_3O_8 by ammonia into UO_2 begins at 550°C, and is completed at about 650°C. It has been noticed that ammonia decomposition occurs at 700°C ; moreover, it is catalysed by UO_2 produced by the reduction of U_3O_8, since no decomposition is observed in the absence of UO_2. Besides, some isothermal experiments carried out at 510°C have confirmed that ammonia reacts directly with U_3O_8, since the shape of the curves obtained either in ammonia or in hydrogen are different: particularly, the reaction is faster with ammonia compared to hydrogen, for the same partial pressure of the reducing gas.

Introduction

The reduction of uranium oxide U_3O_8 to uranium dioxide UO_2 has been studied by temperature programmed thermogravimetry, up to 700°C, the experiments being carried out either in ammonia or hydrogen. The reduction of U_3O_8 by hydrogen has already been studied [1], and a comprehensive modelling of the transformation has been proposed. The comparison between ammonia and hydrogen was done in order to verify if ammonia reacts directly with U_3O_8, or if the reducing gas is hydrogen produced by the decomposition of ammonia, as suggested in the literature [2].

Experimental

The U_3O_8 powder was obtained by calcining in air at 700°C during two hours a UO_3 powder, supplied by Comurhex. It has been verified by X-Ray diffraction that the calcinated powder is composed of U_3O_8, the peaks corresponding to UO_3 having disappeared. The BET surface area of the U_3O_8 powder is 3 $m^2.g^{-1}$ (determined using Kr adsorption at 77K, with a Micromeritics Asap 2000).

The thermogravimetry experiments have been carried out in a TAG24 Setaram thermobalance, at atmospheric pressure, under a flowing gas (total flowrate : 4 $l.h^{-1}$) in which the partial pressures of the gases were controlled by flowmeters (the carrier gas being helium). Experiments have been carried out either in ammonia (P_{NH3} ranging from 35 to 125hPa) or hydrogen (P_{H2} ranging from 42 to 243hPa). The initial mass of the samples was about 35mg.

The gases evolved and consumed during the reduction were followed simultaneously by mass spectrometry (BALZERS QMG 420C).

The X-ray diffraction experiments have been carried out using a diffractometer Siemens D5000 (Cu Kα). In order to determine precisely the position of the diffraction peaks in the UO_2 samples, α-alumina powder was added to the UO_2 powder as an internal standard.

Experimental results

1- Reduction of U_3O_8 by ammonia

A sample of U_3O_8 has been heated up to 700°C (10°C/min) under a flowing mixture of helium and ammonia (P_{NH3}=125 hPa) ; it was maintained at 700°C during 10 minutes, before being cooled down (rate : 10°C/min). The masses m/e 17, 16, 15 (corresponding to ammonia), 28 (nitrogen), 18 (water vapour), and 2 (hydrogen) were followed by mass spectrometry during the whole experiment. The curve of weight loss and the evolution of the various gases versus time are shown in figure 1 (the curve corresponding to the mass m/e=15, characteristic of ammonia only, is not represented here, since the chosen scale is not appropriate (this signal is nearly 100 times lower than the signal corresponding to m/e=16), but its evolution is exactly the same as the evolution of the masses 16 and 17).

The total weight loss is 3.7% (figure 1a), which is slightly lower than the theoretical weight loss corresponding to the reduction of U_3O_8 into UO_2 (3.82%).

It can be noticed that simultaneously to the weight loss linked to the reduction (which begins at about 550°C), ammonia is consumed and nitrogen and water vapour are released (figures 1b and 1c). When the reaction is completed, at about 650°C, the various gases come back to their initial level ; then, during the isothermal step (10 minutes at 700°C), the decomposition of ammonia is observed (decreasing signal for NH_3 (16, 17) and increasing for N_2 (28) and H_2 (2)). However, there is no evolving of water (18), which is in agreement with the decomposition reaction. During the cooling of the sample, all signals come back to their initial level, the decomposition of ammonia stops as soon as the temperature decreases ; no weight loss neither gaseous evolving are observed during the cooling.

This experiment shows that ammonia reacts directly with U_3O_8, the decomposition is observed only at 700°C, when the sample is completely reduced into UO_2. In order to verify that the decomposition is not linked to the reaction of reduction, this sample of UO_2, cooled under ammonia, has been heated up again to 700°C, under the same gaseous atmosphere (ammonia and helium) : the results are indicated in figure 2. The decomposition of ammonia is observed as soon as the temperature reaches 700°C and during the isothermal step (30 minutes), but it no longer occurs when the temperature decreases. Moreover, a similar experiment carried out in the same conditions of temperature and pressure, but without any sample, has shown that the decomposition of ammonia does not occur (which is in agreement with the literature data [3,4], since at this temperature the decomposition is observed only in the presence of metallic catalysts).

From these experiments, it can be concluded that ammonia decomposition is not due to the reaction of reduction, and that uranium dioxide UO_2 is a catalyst for this decomposition.

2- Comparison between the reduction curves in ammonia and hydrogen

In order to compare the effect of ammonia and hydrogen, an experiment has been carried out up to 700°C (10°C/min) under flowing helium and hydrogen (P_{H2}=85 hPa). Figure 3 shows the curves of weight loss and rate of weight loss obtained under ammonia (125 hPa) and hydrogen (85 hPa) : U_3O_8 reduction occurs in the same temperature range and with a similar rate for the two gases, the weight loss obtained under hydrogen being slightly higher (3.89% instead of 3.7%).

Some isothermal experiments have also been carried out, at 510°C, the reducing gas being introduced in the thermobalance when the temperature is stabilised (as shown by the arrow in figure 4).

Figure 4 shows a curve obtained at 510°C under 125 hPa of ammonia : a rapid weight loss is observed firstly, then the rate decreases, passes through a maximum and decreases again. The final weight loss is 3.41%, which is lower than the theoretical weight loss. However, the reaction seems to be completed, since the sample mass remains constant after 40 minutes at 510°C. XRD experiments have shown that both U_3O_8 and UO_2 are observed in a sample cooled after the first weight loss ($\Delta m=0.5\%$), and that a sample analysed at the end of the reaction exhibits only the UO_2 peaks.

The effect of the partial pressure of ammonia is illustrated in figure 5, which shows the curves obtained under 125 hPa and 42.5 hPa : an accelerating effect of ammonia is observed after the first weight loss.

A comparison of the curves obtained under ammonia and hydrogen, with the same partial pressure (42.5 hPa), is given in figure 6a, the curves representing the rate $d(\Delta m)/dt$ versus the weight loss are represented in figure 6b. It can be noticed that the reduction is faster in ammonia, but that the total weight loss obtained in hydrogen is higher (3.8%), in agreement with the theoretical weight loss.

Despite the fact that the shape of the curves is quite different, it can be observed, in both cases, a first maximum of the rate (for a weight loss lower than about 0.6%), then a second maximum, the inflexion point being situated at about $\Delta m=2.3\%$ for ammonia and 0.7% for hydrogen.

In order to explain the difference in the final weight loss for samples reduced under ammonia (≈3.4%) or hydrogen (≈3.8%), XRD experiments have been performed on the two samples resulting from the experiments shown in figure 6. If we assume that the uranium dioxide obtained under ammonia is a non-stoichiometric UO_{2+x} oxide, the experimental weight loss (3.41%) would correspond to a value of x equal to 0.07 and the diffraction peaks should be shifted towards higher angles.The positions corresponding to $UO_{2,07}$ can be calculated knowing the cell parameter « a » for UO_2 (a=5.467 Å, JCPDS file 41-1422) and $UO_{2.25}$ (a=5.441 Å, JCPDS file 20-1344). Assuming that a is a linear function of x (Vegard's law), the cell parameter a for $UO_{2.07}$ would be equal to 5.459 Å. Then, the d_{hkl} distances and the corresponding angles can be evaluated, they are reported in table 1.

Figures 7a and 7b show the diffractograms obtained for the two samples reduced under ammonia or hydrogen, the positions of the peaks for UO_2 and $UO_{2.07}$ being indicated (some peaks corresponding to α-alumina used as a standard are observed too). The experimental values of the peak positions are reported in the two last columns of table 1 for both samples. The expected shift between UO_2 and $UO_{2.07}$ being small, it may be quite difficult to detect experimentally. Nevertheless, considering the peaks magnified in figures 7a and 7b and the values given in table 1, it can be concluded that the peaks corresponding to the sample reduced under ammonia are not significantly shifted compared to those of the sample reduced in hydrogen and do not correspond to $UO_{2.07}$. Thus, it seems that the experimental weight loss obtained in ammonia can not be accounted for by the formation of a non stoichiometric UO_{2+x}.

This weight loss could also have been due to ammonia adsorption at the surface of the UO_2 oxide, but none of the bands characteristic of ammonia have been detected by infra-red spectroscopy experiments.

Further investigations are being performed in order to explain this experimental weight loss, and the shape of the kinetic curves.

Conclusions

The reduction of U_3O_8 by ammonia has been studied by thermogravimetry and mass spectrometry. It has been shown that U_3O_8 is reduced directly by ammonia, which is not decomposed during the reduction process. Ammonia decomposition occurs in our experimental conditions at about 700°C, only in the presence of uranium dioxide UO_2, which acts as a catalyst (no decomposition is observed without UO_2).

Isothermal experiments at 510°C have confirmed that ammonia reacts directly with U_3O_8, since the shape of the curves obtained either in ammonia or in hydrogen are different ;

besides, the reaction is faster with ammonia compared to hydrogen, for the same partial pressure of the reducing gas.

Finally, it has been noticed that the final weight loss obtained in ammonia (about 3.4%) is always lower than the theoretical one (3.82%). XRD experiments seem to show that this result cannot be accounted for by the formation of a non stoichiometric uranium dioxide UO_{2+x} ($UO_{2.07}$). Further investigation are necessary to elucidate this point.

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FIGURE CAPTIONS

Figure 1: Heating of U_3O_8 under ammonia (700°C, 10°C/min, P_{NH3}=125 hPa) ; weight loss curve (a) and evolved gas (b-c).

Figure 2: Evolved gas during the heating (700°C, 10°C/min) and the cooling of UO_2 in ammonia (P_{NH3}=125 hPa).

Figure 3: Heating of U_3O_8 (700°C, 10°C/min) under ammonia (P_{NH3}=125 hPa) or hydrogen (P_{H2}=85 hPa) ; curves of weight loss and rate of weight loss.

Figure 4: Curves of weight loss and rate of weight loss versus time in isothermal conditions (T=510°C) , in ammonia (P_{NH3}=125 hPa).

Figure 5: Effect of the ammonia partial pressure on the reduction of U_3O_8 at 510°C.

Figure 6: Comparison of the curves obtained in ammonia (42.5 hPa) or hydrogen (42.5 hPa) ; weight loss versus time (a) and rate of weight loss versus weight loss (b).

Figure 7: Diffractograms of uranium dioxide samples obtained from the reduction of U_3O_8 by ammonia or hydrogen ; 2θ angle ranging from 27 to 34 (a), and 46 to 60 (b).

TABLE CAPTION

Table 1 : Positions of the diffraction peaks for UO_2 (JCPDS file 41-1422) and $UO_{2.07}$ (calculated) and positions of the experimental diffraction peaks observed in the samples reduced under hydrogen or ammonia.

	UO_2		$UO_{2.07}$		Experimental (H_2)	Experimental (NH_3)
[hkl]	d_{hkl} (Å)	2θ	d_{hkl} (Å)	2θ	2θ	2θ
[111]	3.153	28.28	3.152	28.29	28.26	28.27
[200]	2.733	32.74	2.729	32.78	32.74	32.74
[220]	1.933	46.97	1.930	47.04	46.97	46.99
[311]	1.647	55.75	1.646	55.81	55.72	55.74
[222]	1.578	58.43	1.576	58.52	58.43	58.47

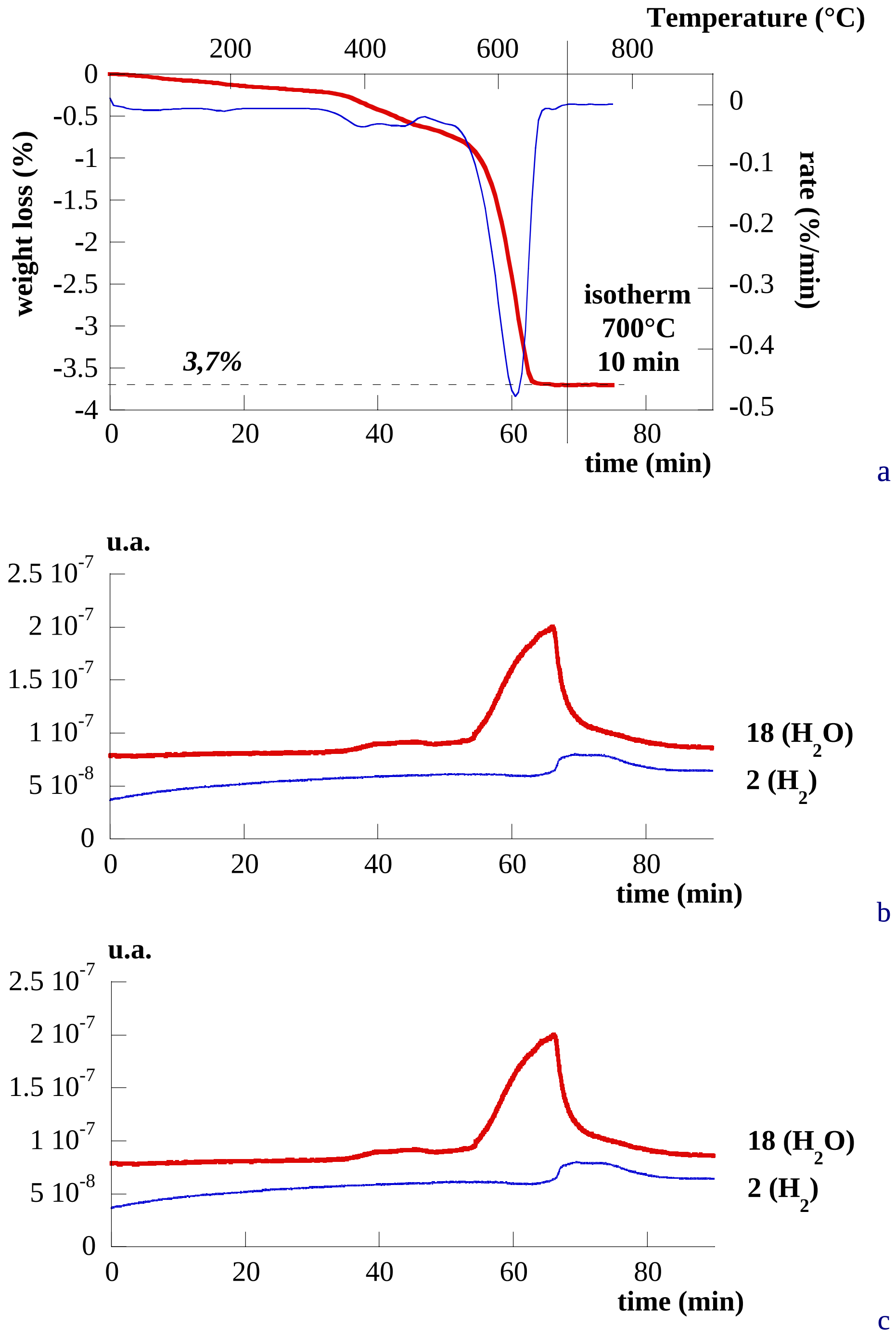
Temperature (°C)
200
400
600
800
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
weight loss (%)
0
-0.1
-0.2
-0.3
-0.4
-0.5
rate (%/min)
3,7%
isotherm
700°C
10 min
0
20
40
60
80
time (min)
a
u.a.
2.5 10-7
2 10-7
1.5 10-7
1 10-7
5 10-8
0
18 (H2O)
2 (H2)
0
20
40
60
80
time (min)
b
u.a.
2.5 10-7
2 10-7
1.5 10-7
1 10-7
5 10-8
0
18 (H2O)
2 (H2)
0
20
40
60
80
time (min)
c

Figure 1:

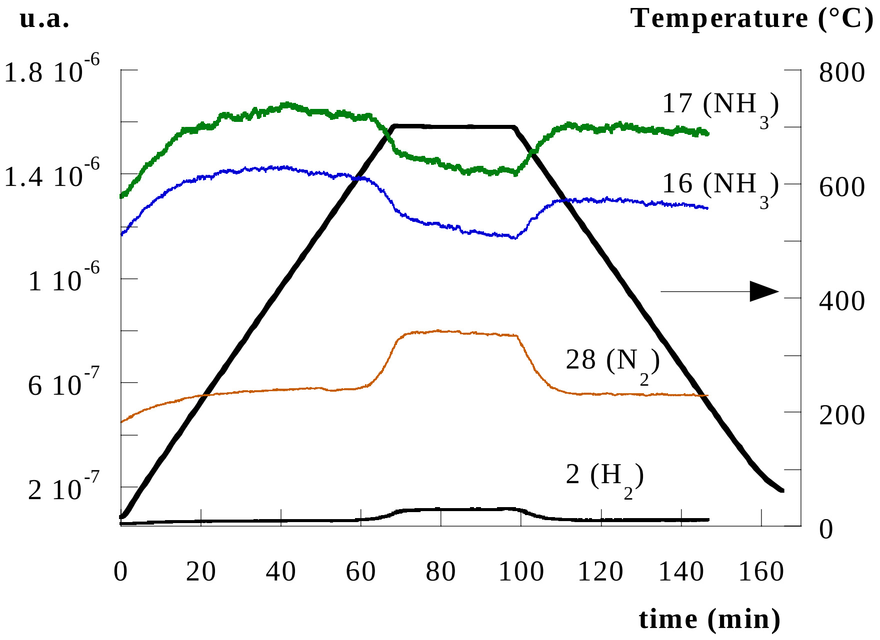

Figure 2:

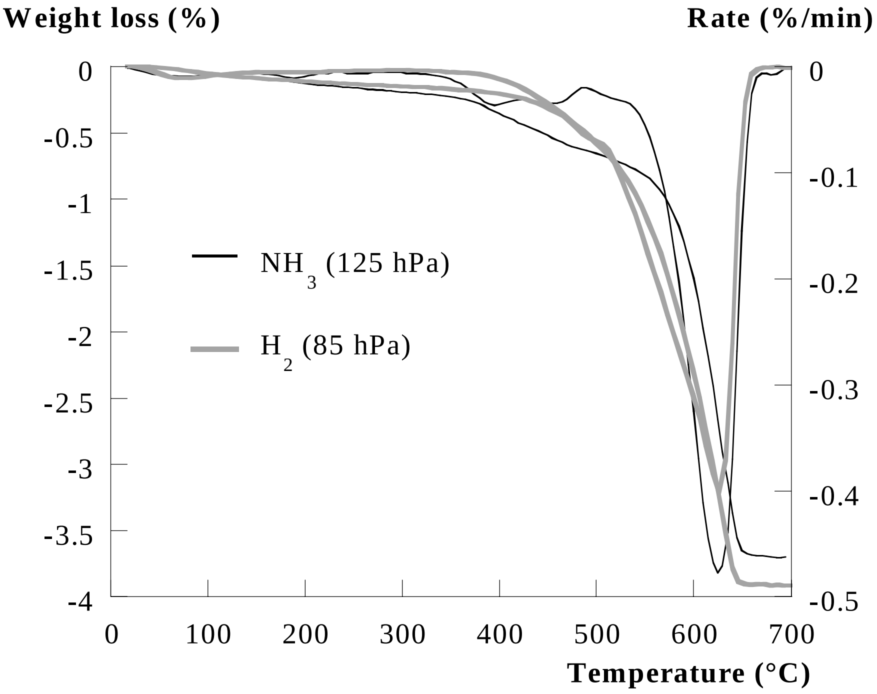

Figure 3:

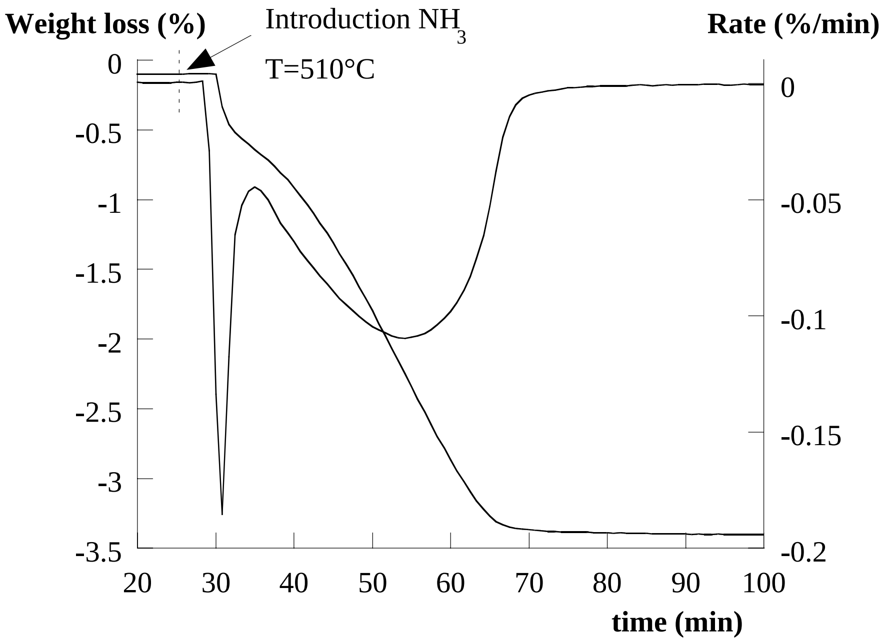

Figure 4:

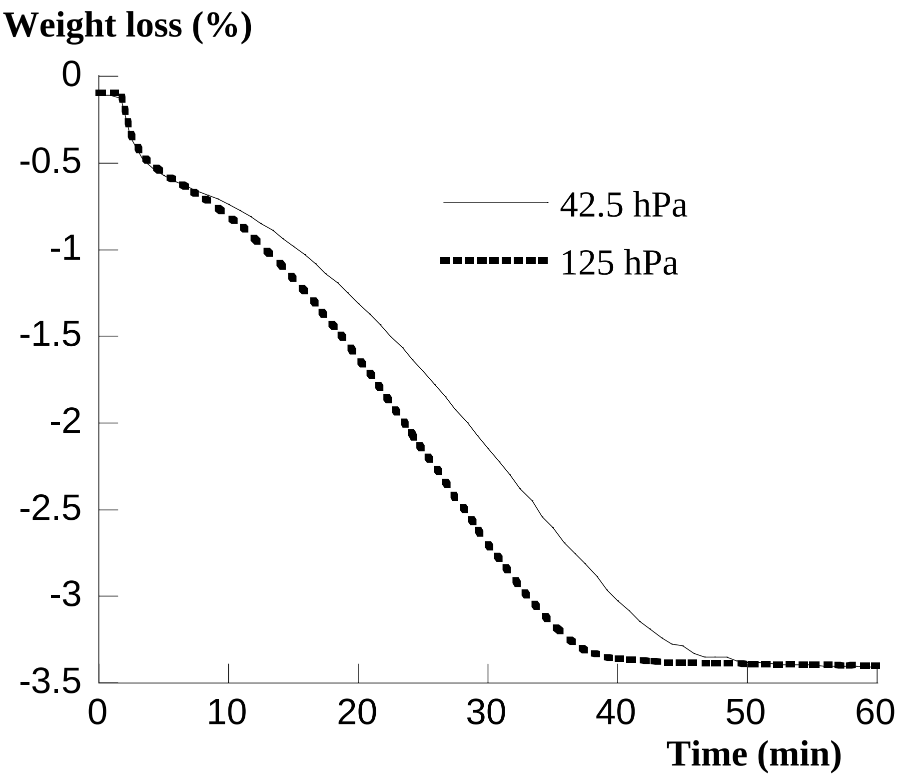

Figure 5:

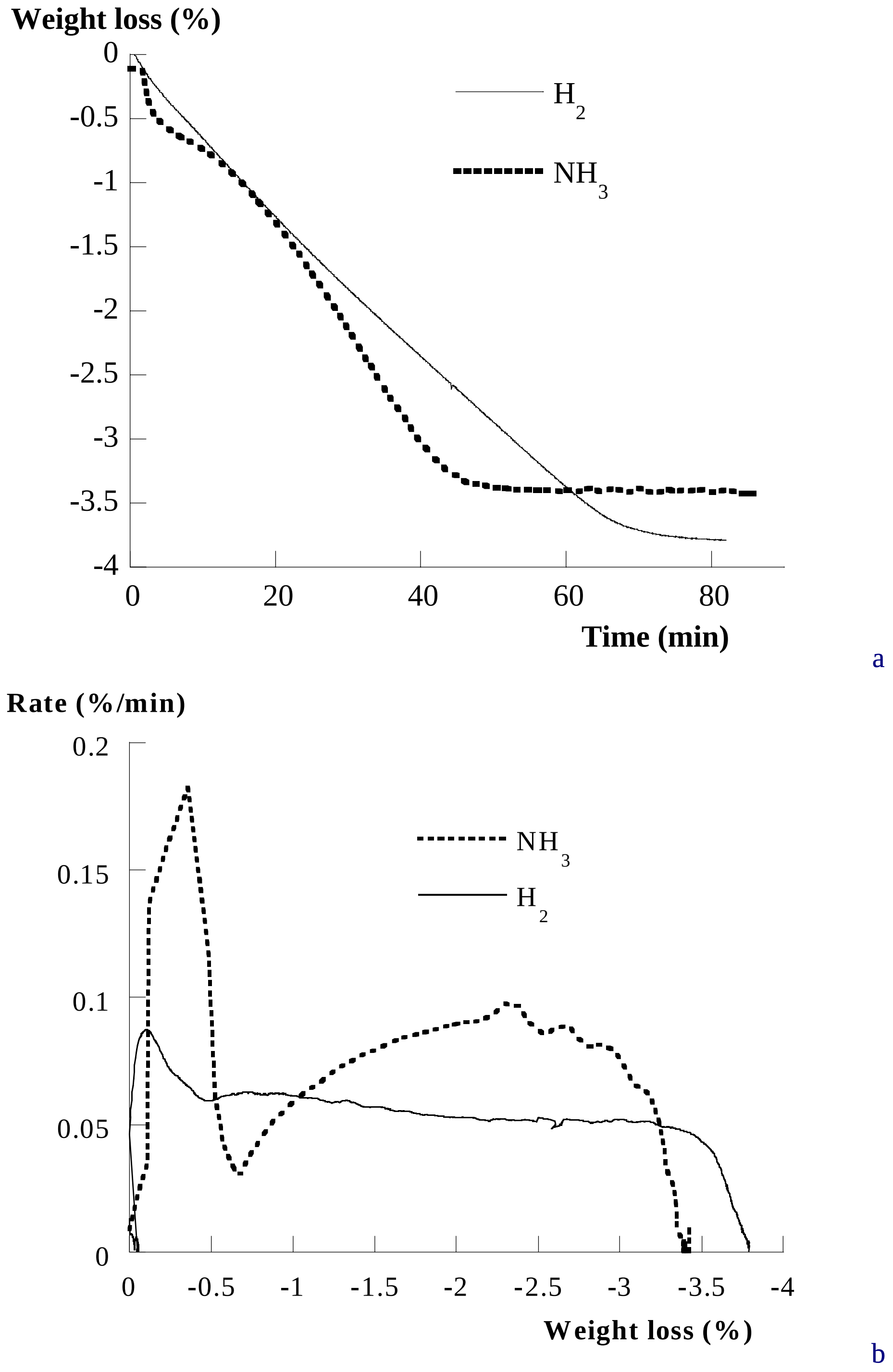
Weight loss (%)
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
0
20
40
60
80
Time (min)
H_2
NH_3
a
Rate (%/min)
0.2
0.15
0.1
0.05
0
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
Weight loss (%)
NH_3
H_2
b

Figure 6:

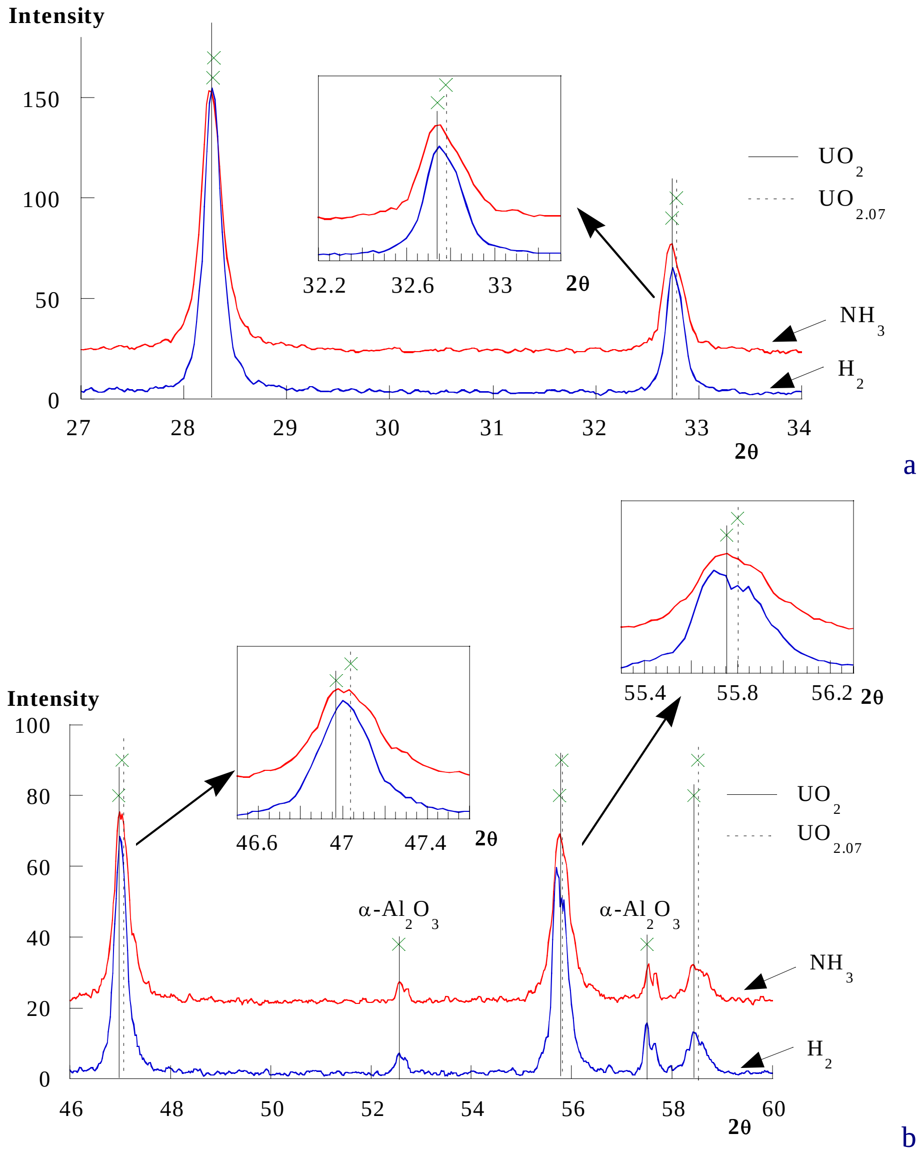
Intensity
150
100
50
0
27
28
29
30
31
32
33
34
2θ
32.2
32.6
33
2θ
UO2
UO2.07
NH3
H2
a
Intensity
100
80
60
40
20
0
46
48
50
52
54
56
58
60
2θ
46.6
47
47.4
2θ
55.4
55.8
56.2
2θ
α-Al2O3
α-Al2O3
UO2
UO2.07
NH3
H2
b

Figure 7: