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Catherine Brun, Michèle Pijolat, Michel Soustelle, Françoise Valdivieso. The influence of hydration of uranium trioxide on its following reduction by hydrogen into uranium dioxide UO2. Eurosolid 4 : European conference on transformation kinetics and reactivity of solids, Sep 1997, Saint Vincent, Italy. pp.75-80. emse-00614959

HAL Id: emse-00614959

https://hal-emse.ccsd.cnrs.fr/emse-00614959

Submitted on 17 Aug 2011

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THE INFLUENCE OF HYDRATION OF URANIUM TRIOXIDE ON ITS FOLLOWING REDUCTION BY HYDROGEN INTO URANIUM DIOXIDE UO_2

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Abstract

The reduction of U_3O_8 by hydrogen has been studied by thermogravimetry in the range 510-600°C and 1-40 kPa. The kinetic curves have been interpreted by a new model involving the steps of nucleation and growth. This allowed to determine the variations of the frequency of nucleation and of the specific rate of growth as a function of hydrogen pressure and temperature. The influence on the kinetics of the hydration of UO_3 prior to its reduction by hydrogen could also be explained due to the same model.

Introduction

The reduction of uranium trioxide into uranium dioxide can be achieved by means of a gas-solid reaction in which hydrogen is contacted to the oxide powder at high temperature. It is known [1-2] that this transformation occurs in two steps : the uranium trioxide is first converted into U_3O_8 phase, which in turn reacts with hydrogen to give the UO_2 phase. In a previous study [3], we have shown that it was interesting to separate both the reactions in order to well understand the mechanism of formation of UO_2 from U_3O_8. Using a kinetic study at fixed temperature, 510°C, and hydrogen pressures, it was possible to interpret the shape of the kinetic curves by a model in which the rate-limiting step of the growth process is located at the external interface (i.e. the surface of the particles), while the nucleation process occurs as soon as the experimental conditions are reached. Moreover the variations of the experimental specific rate of growth as a function of the hydrogen pressure were found to be in agreement with a mechanism of reduction involving the desorption of water as the rate-limiting step.

However, we noticed that in the case of hydrogen pressures higher than 13 kPa, the kinetic experimental curves were fitted by assuming that the ratio between the molar volumes of the initial and final oxides was different from the theoretical one, the higher its value the higher the pressure . This was not really explained, if not by a probable change in the porosity of the UO_2 layer. This paper will present a more fully complete model of the transformation than in the previous article, which accounts for the various shapes of the experimental kinetic curves even at higher temperatures and hydrogen pressures.
Moreover, the influence, on the kinetics of reduction, of the hydration of the uranium trioxide previous to its reduction will be examined, and interpreted in terms of changes in both geometrical and intrinsic reactivity changes.

1. Samples and experimental methods

Samples of UO_3, supplied by Comurhex, exhibit an initial BET surface area equal to 15 m^2g^{-1}. UO_3 was converted into U_3O_8 in situ in a TAG24 Setaram thermobalance by calcination under flowing oxygen at 800°C during three hours. The surface area of U_3O_8 prior to reduction by hydrogen is equal to 2.3 m^2g^{-1}. The mean radius of equivalent non porous spherical particles is thus found to be equal to 0.16 µm.
The isothermal kinetic curves have been obtained in the range 510-600°C as previously described, with two successive reductions, using a flowing mixture of hydrogen, water vapour and helium [3].

The hydration of the uranium trioxide consisted in reacting 7 kPa water vapour and the oxide powder at 55°C during two days in order to obtain uranyl hydroxide, $UO_2(OH)_2$, as verified by X-ray-diffraction. Once prepared, this sample is then calcined in the thermobalance in the same conditions than uranium trioxide in order to obtain U_3O_8. The surface area of the U_3O_8, noted in the following U_3O_8-H is equal to 1.7 m^2g^{-1}. It corresponds a mean radius of 0.21 µm on the assumption of non porous spherical particles.

2. Experimental results

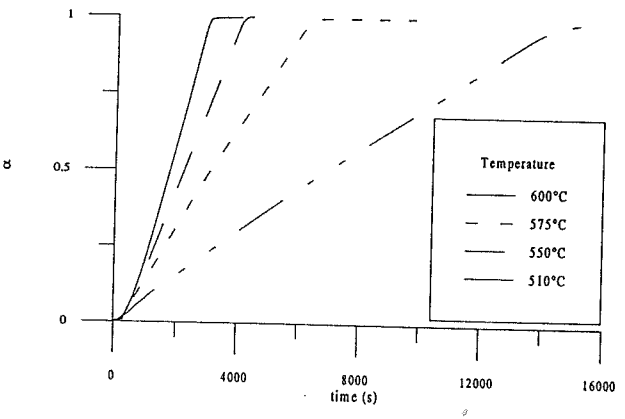


Figure 1.
Extent of conversion versus time of U_3O_8 sample at various temperatures and 2.2 kPa.

The kinetic curves of the fractional conversion (α) versus time deduced from the thermogravimetry experiments are displayed in Figure 1 in the case of various temperatures of reduction and 2.2 kPa of hydrogen pressure. The shape of the curves varies from an approximately decelerating behaviour towards an accelerating one. Moreover, it can be noticed in the case of temperatures superior or at least equal to 550°C that there is an inflexion point, which seems to indicate that the simple kinetic model used to interpret the data obtained at 510°C will no more be adequate.

In Figure 2 are shown the curves corresponding to the reduction of the U_3O_8-H sample in various conditions of hydrogen pressure at 510°C. It can be seen that the hydration of uranium trioxide prior to its reduction into UO_2 modifies the rate at which the transformation proceeds.

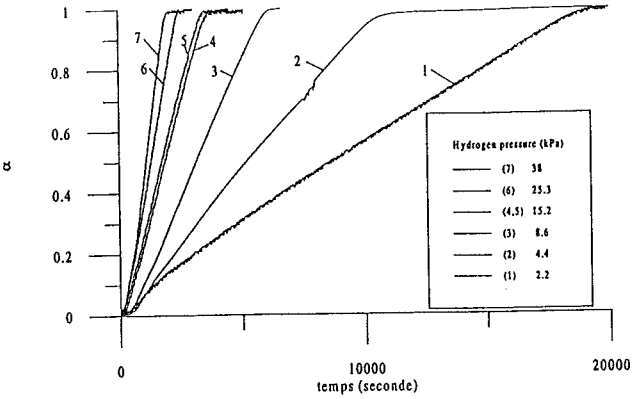


Figure 2. Extent of conversion versus time of U_3O_8-H sample at 510°C for various partial pressures of hydrogen

3. Interpretation of the kinetic curves

In order to interpret all the experimental curves, that is to say in the range of temperature and pressure investigated in this study, we propose a new model which involves both the nucleation and growth processes. A slightly similar model has already been published in the case of the dehydration of the lithium sulphate [4] to account for sigmoïdal shapes of the kinetic curves. It was assumed that the nuclei can appear at a given frequency, γ, at the surface of non yet transformed particles of U_3O_8, while once a nucleus has been formed, the anisotropy of the growth rate is such than a very thin layer of UO_2 is formed instantaneously compared to the radial growth towards the centre of the particle. In the previous model, the rate-limiting step of the growth process was assumed to be located at the interface between the UO_2 layer and the U_3O_8 core, like in the sphere contracting model if one consider the transformation of a unique particle.

In the present reaction, such a location of the rate-limiting step is difficult to admit because in the case of curves obtained at 510°C and moderate hydrogen pressures, we already shown that the rate-limiting step of growth could only occur at the external interface, i.e. the surface of the nucleated particles (after nucleation, these are covered by UO_2). So we have taken the same assumptions of the model proposed for the dehydration of the lithium sulphate, except that of the location of the rate-limiting step of growth, that we have replaced by the surface of the particles.

The comparison of the experiments to the model can be achieved as previously by calculating in both cases « reduced » rates : they are the ratio of the rate to its value for α equal to 0.5. Then the experimental reduced rate is plotted versus a for each experiment. From the model we get the variations of the fractional conversion as a function of a dimensionless time, θ, defined as below in equation (1), and those of the theoretical rate $d\alpha/d\theta$. A parameter, A, which varies as γ/v, according to equation (2), where v is the specific rate of growth, enters in the theoretical rate and its value allows the adjustment between experiment and model :

$$\theta = \frac{V_{m_{U_3O_8}} . v}{3 . r_0} . t \qquad (1)$$

$$A = \frac{4\pi r_0^3 . \gamma}{\frac{V_{m_{U_3O_8}}}{3} . v} \qquad (2)$$

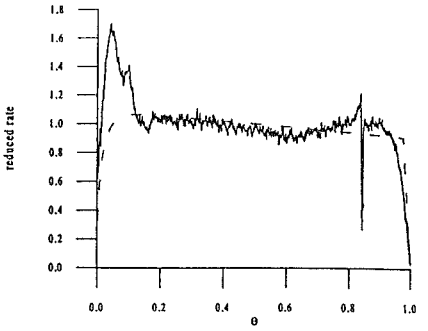


Figure 3a. Experimental (—) and calculated (--) reduced rates in the case of U_3O_8 sample at 510 °C and 1.1 kPa of hydrogen; A=100 (see text)

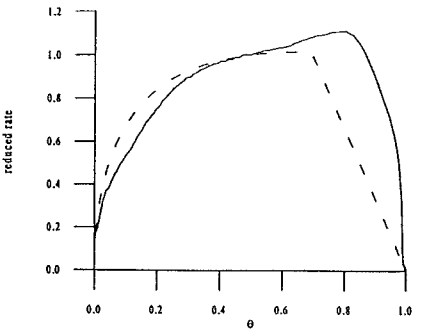


Figure3b. Experimental (—) and calculated (--) reduced rates in the case of U_3O_8 sample at 600 °C and 13.7 kPa of hydrogen; A=8 (see text)

In Figure 3 we show for two experimental conditions the result of the best fits between the theoretical and experimental reduced rates curves. Once the value of A determined from the best agreement between experimental and theoretical reduced rates, the linear relation between θ and t (cf. equation (1)) is checked and then its slope can be determined. From the knowledge of the initial radius of the particles of U_3O_8 (0.16 μm) and its molar volume (100.35 cm^3mole^{-1}), this allows the determination of the values of the specific rate of growth in each experiment. Using the values of the parameter A, and equation (2), we obtain easily the related values of the specific frequency of nucleation.

The variations of γ and ν are shown in Figure 4 and 5 respectively as a function of hydrogen pressure (at 510°C) and for various temperatures.

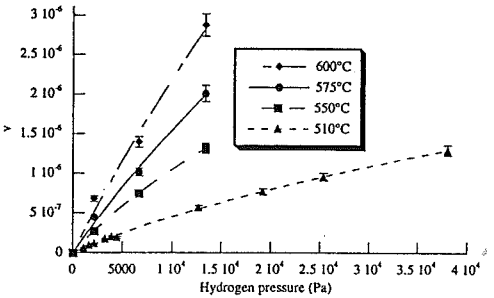


Figure 4. Variation of the specific rate of growth versus hydrogen partial pressure for U_3O_8 sample at various temperatures.

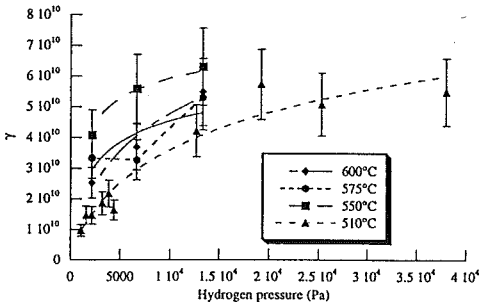


Figure 5. Variation of the specific frequency of nucleation versus hydrogen partial pressure for U_3O_8 sample at various temperatures

We have verified that in the case of 510°C the values of v such obtained are very close to those that were previously determined (3). This is not surprising since the nucleation and anisotropic growth model is able to predict continuously decelerating kinetic curves when the value of the parameter A becomes higher than 100. This means that in such conditions the nucleation process can be considered as instantaneous compared to the time required to transform one particle.

If we consider the experimental variations of v with the partial pressure in hydrogen in the whole range of temperature investigated, we obtain a good agreement with the law given in equation (3), which was deduced from the mechanism previously published, in the case of the desorption of water as the rate-limiting step of growth [3] :

$$v = k_2 \frac{K_1 K_4^{1/4} . P_{H_2}}{\left(1 + K_1^{1/2} K_4^{1/8} . \sqrt{P_{H_2}}\right)^2} . \left(1 - \frac{\frac{P_{H_2O}}{P_{H_2}}}{K_1 K_2 K_4^{1/2}}\right) \quad (3)$$

We have also found that the frequency of nucleation (Figure 5) fits rather well such a law, which indicates that probably in the mechanism of nucleus formation there is a similar step which is rate-limiting as well as for the growth.

4. Interpretation of the influence of the hydration of UO_3 on the reduction

The experimental kinetic curves obtained in the case of the UO_3-H sample have been interpreted by means of the above model, and thus the values of the frequency of nucleation as well as those of the specific rate of growth have been determined. In this part, we have used of course the value of 0.21 µm for the radius of the initial particles.
The results are plotted in Figure 6 : it can be seen that the specific rate of growth, v, is found to be very close to that of the UO_3 initial sample, while the frequency of nucleation, γ, is quite some different.

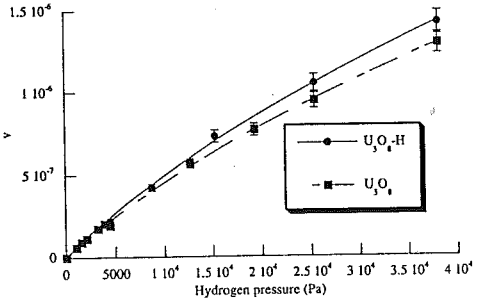


Figure 6. Comparison of the specific rate of growth of U_3O_8 and U_3O_8-H samples as a function of hydrogen partial pressure at 510°C.

We can thus interpret the inhibiting effect of the hydration of UO_3 on its subsequent behaviour in reduction as a consequence of both changes :

* one is strictly related to the differences in the particle size from one sample to another,
* the other is due to a difference in the frequency of nucleation, which depends of the intrinsic properties of the oxide ; this suggests that some surface defects involved in the nucleation process are modified by the past history of the solid.

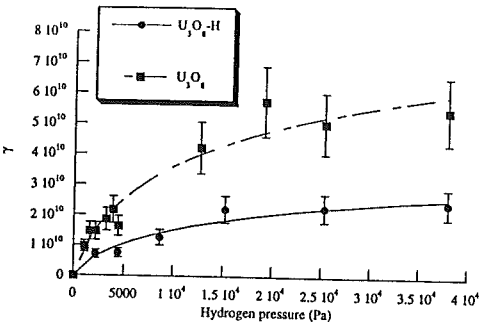


Figure 7. Comparison of the specific frequency of nucleation of U_3O_8 and U_3O_8-H samples as a function of hydrogen partial pressure at 510°C.

Conclusion

The kinetics of the reduction of U_3O_8 by hydrogen in a range of temperatures (510-600°C) and pressures (1-40 kPa) has been interpreted by means of a model of nucleation and anisotropic growth. The variations of the frequency of nucleation and of the specific rate of growth have been obtained and found to be in agreement with a rate-limiting step of desorption of water from the surface of the particles.
The influence of the hydration of UO_3 prior to the reduction has been explained due to the same model by a change in the initial size of the particle and a modification of the nucleation frequency.

Acknowledgement

This work has been supported by Comurhex with the contribution of the ANRT (CIFRE grant).

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