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The influence of particle size on the kinetics of UO_2 oxidation in aqueous powder suspensions

Olivia Roth [*], Tobias Bönnemark, Mats Jonsson

School of Chemical Science and Engineering, Nuclear Chemistry, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

Abstract

Previous studies have indicated that the rate of a heterogeneous liquid–solid reaction depends on the size of the solid particles. It has been suggested that both the pre-exponential factor and the activation energy depend on the particle size. The processes involved in dissolution of UO_2 have been extensively studied because of their importance for the safety analysis of a future deep repository for spent nuclear fuel and in many of these studies powder suspensions of UO_2 are used as a model system. Therefore, it is of importance to investigate and quantify the particle size effect on the kinetics of UO_2 oxidation in order to enable comparison of data from studies on different solid substrates. In this work the influence of particle size on the second order rate constant and on the activation energy of the reaction between MnO_4^- and UO_2 was studied using aqueous UO_2-particle suspensions of four different size distributions. A comparative study of the activation energy for the reaction using a UO_2 pellet was also performed.
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1. Introduction

The processes involved in dissolution of UO_2 have been extensively studied because of their importance in the safety analysis of a future deep repository for spent nuclear fuel. The release of many radioactive species from the spent fuel is governed by the dissolution of the UO_2-matrix [1]. Under reducing conditions, the solubility of U(IV) is low. The solubility of U(VI) is, however, significantly higher and oxidation of the UO_2 matrix will,

therefore, increase its solubility [2]. Normally, the deep repository conditions are expected to be reducing, but if ground water comes in contact with the spent fuel a number of oxidizing species are formed by radiolysis of the water, e.g. H_2O_2, O_2, $OH^·$, $CO_3^{·-}$ and $HO_2^·$ [3]. If and how these radiolysis products will affect the rate of dissolution of the spent fuel are questions that have been discussed for several decades [1].

The deep repository is a very complex system with numerous factors involved in determining the dissolution rate of the UO_2 matrix. To circumvent this problem, the employment of numerical models and simulations, based on elementary reactions involved in the system, is necessary. A prerequisite for a reliable modeling is high quality input data,

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[*] Corresponding author. Tel.: +46 8 790 92 79; fax: +46 8 790 87 72.

E-mail address: oliviar@kth.se (O. Roth).

i.e. kinetics and mechanisms for these elementary reactions, topics that have the been subject of recent studies [4–7].

In these studies, UO_2-powder suspensions are often used as model substances for spent nuclear fuel. These powder suspensions are useful as model systems, since the larger surface to volume ratio and the flexibility of the system allow determination of pseudo first order and second order rate constants. However, the reactivity of the UO_2 powder is not expected to be identical to the reactivity of spent fuel for a number of reasons. One difference is that the spent fuel contains impurities in form of fission products and transuranium elements, which are radioactive and expose the fuel to constant self-irradiation. Furthermore, physical properties such as grain size and porosity are changed when irradiating the fuel in the reactor [8,9]. Another difference between the powders and the pellets is the particle size.

It has been shown that in the case of oxidation of magnetite, the particle size does have an influence on the rate of the reaction. Furthermore, it was suggested that both the pre-exponential factor and the activation energy strongly depend on the particle size [10]. It is of importance to investigate and quantify this effect in the case of UO_2 in order to enable comparison of data from studies on different solid substrates and to relate data from kinetic studies performed on powder suspensions to the kinetics for fuel pellets.

According to the theory presented in [11], the complete rate expression for this type of system (assuming spherical geometry of the particles) is given by:

$$\frac{d[Ox]}{dt} = -\frac{2k_B T}{3\pi\eta} \frac{R_{MOX}^2}{R_{OX}R_p} \left(e^{-\frac{E_a}{RT}}\right)[Ox]\frac{N_{MOX}}{V}, \qquad (1)$$

where k_B, T and η denote the Boltzmann constant, the temperature and the viscosity of the solvent, [Ox] denotes the concentration of oxidant in solution, R_p denotes the particle radius and R_{OX} and R_{MOX} are the molecular radius of the oxidant and the solid material, respectively. N_{MOX} denotes the number of solid phase molecules on the particle surface being exposed to the solution of volume V.

Eq. (1) describes the particle size dependence of the pre-exponential factor. In a recent study of the reaction between iron oxides and H_2O_2 it was suggested that also the activation energy is strongly dependent on particle size and it was proposed

that the dependence could be described by Eq. (2) [10]

$$-\Delta E_a = k_B T \ln\frac{n_s}{n_b}, \qquad (2)$$

where n_s and n_b denote the number of molecules on the surface and the total molecule content of the particle, respectively. This equation originates from the fact that larger particles contain more electrons than smaller particles relative to the number of surface sites (the electron content increases with r^3 while the number of surface sites increases with r^2) and that a large pool of electrons would lower the barrier for removal of electrons. Hence, the activation energy should decrease with increasing particle size. Using the Boltzmann distribution the particle size dependence of the activation energy can then be expressed by Eq. (2).

In this work we have performed a quantitative study of the effect of particle size on the kinetics of the reaction between MnO_4^- and UO_2. The particle size influence on the second order rate constant and on the activation energy was studied using aqueous UO_2-particle suspensions of four different size distributions. A comparative study of the activation energy for the reaction using a UO_2 pellet was also performed.

2. Experimental

The UO_2-powder and the UO_2-pellet were supplied by Westinghouse Atom AB. Other chemicals were supplied by Merck and AGA. Millipore Milli-Q filtered water was used throughout.

The powder was sieved into four different size fractions, <20 μm, 20 μm–41 μm, 41 μm–72 μm and >72 μm. Each fraction was washed with 10 mM $NaHCO_3$ prior to the experiments in order to remove U(VI) from the surfaces. The amount of suspended UO_2 was varied between 20 mg and 40 mg and the volume between 20 mL and 100 mL in the experiments determining the second order rate constant. In the activation energy study, 20 mg UO_2 in 100 mL suspension was used and the temperature was varied between 0 °C and 73 °C.

The suspensions containing 10 mM $NaHCO_3$ and approximately 0.7 mM MnO_4^- were purged with Argon throughout the experiment and stirred by a magnetic stirrer. Samples were taken regularly during 5–10 min, sample volume 2–3 mL. In order to stop the reaction and clear the solution the sample was filtered (pore size 0.2 μm) before analysis.

The concentration of MnO_4^- was measured by UV/visible spectroscopy at 525 nm (Jasco V-530 UV/VIS-Spectrophotometer).

The specific surface area of each powder fraction was measured using the BET isotherm. The BET equipment used was Micromeritics Flowsorb II 2300 with 30% N_2 in Helium. In order to further characterize the surfaces, Scanning Electron Microscopy was used on fractions 1 ($>72\,\mu m$) and 4 ($<20\,\mu m$).

In the UO_2-pellet experiments, 10 mL to 0.5 mM MnO_4^- solutions containing 10 mM $NaHCO_3$ were used. The solutions were purged with Argon throughout the experiment and stirred by a magnetic stirrer. Samples were taken every 5 min, sampling volume ~2 mL. The samples were analysed with UV/Vis spectroscopy at 545 nm and 390 nm (Jasco V-530 UV/VIS-Spectrophotometer) and then poured back into the reaction vessel. In previous experiments performed using this system we found that Mn(IV) was formed during the reactions, which interfered with the measurement of Mn(VII) (545 nm). Therefore, also the Mn(IV) concentration was measured (390 nm) and the Mn(VII) concentrations were corrected, with respect to the Mn(IV) measurements. The temperature was varied between 25 °C and 75 °C.

3. Results and discussion

The experimentally determined second order rate constant for each size fraction, determined from the slope when plotting the pseudo-first order rate constant versus the surface to volume ratio [5], is given in Table 1. In Fig. 1 the second order rate constants are plotted as a function of the inversed particle radius. It should be noted that the approximate mean radii of the particles are only estimates, and that the subsequent results from calculations based on these radii will be somewhat uncertain since we will always have a distribution of particle sizes within each fraction.
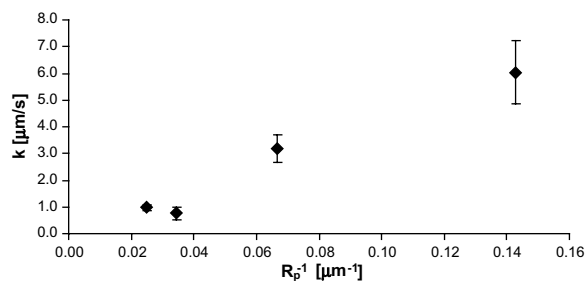

Fig. 1. Experimentally determined second order rate constants for the reaction between UO_2 and MnO_4^- plotted versus R_p^{-1} for four size fractions of UO_2 powder.

Judging from Eq. (1), we would expect the rate constants to be inversely proportional to the particle size, provided that the activation energy is constant. Our experimental data seem to follow this trend quite well, as can be seen in Fig. 1. However, the experimentally determined activation energies are not independent of particle size. As can be seen in Table 2, there is a significant difference in the experimental activation energy among all fractions except fraction 3 and 4. The relative theoretical activation energies (using fraction 2 as reference) are calculated from Eq. (2) and given in Table 2. When compared to the experimental data, we find that they seem to follow the same trend.

Taking the calculated activation energies into account, we can calculate the relative (i.e. normalized with respect to fraction 2) theoretical rate constants from Eq. (1). For comparison the experimentally determined rate constants also have been normalized with respect to fraction 2; the results are given in Table 3. As can be seen for the relative theoretical rate constant, the particle size dependence of the activation energy cancels out the particle size dependence of the pre-exponential factor (in this particle size range). Hence, on the basis of Eqs.

Table 1
Experimentally determined second order rate constants for the reaction between UO_2 and MnO_4^- and approximate radii for four size fractions of UO_2 powder

Fraction	Particle radius (μm)	k (m/s)
1 ($>72\,\mu m$)	40	$(10 \pm 1) \times 10^{-7}$
2 (41–72 μm)	29	$(8 \pm 3) \times 10^{-7}$
3 (20–41 μm)	15	$(3.2 \pm 0.5) \times 10^{-6}$
4 ($<20\,\mu m$)	7	$(6 \pm 1) \times 10^{-6}$

Table 2
Experimentally determined and theoretically calculated activation energies for the reaction between UO_2 and MnO_4^- for four size fractions of UO_2 powder

Fraction	E_a experimental (kJ/mol)	ΔE_a experimental (kJ/mol)	ΔE_a theoretical (kJ/mol)
1 ($>72\,\mu m$)	8.9 ± 3.5	-5.2 ± 3.5	-0.73
2 (41–72 μm)	14.2 ± 1.4	0.0 ± 1.4	0.00
3 (20–41 μm)	18.6 ± 1.6	4.5 ± 1.6	1.50
4 ($<20\,\mu m$)	18.8 ± 1.5	4.6 ± 1.5	3.22

Table 3
Second order rate constants for the reaction between UO_2 and MnO_4^- for four size fractions of UO_2 powder. Experimental rate constants, based on BET surface and geometrical surface respectively, compared with theoretical rate constants

Fraction	k experimental (BET-surface)	k experimental (geometrical surface)	k theoretical
1 (>72 μm)	1.3	1.8	0.9998
2 (41–72 μm)	1.0	1.0	1.0000
3 (20–41 μm)	4.2	2.2	1.0003
4 (<20 μm)	7.9	1.9	1.0006

(1) and (2) we would not expect any difference in reactivity between the size fractions. This is not consistent with our experimental data. One explanation for the disagreement could be that the experimental rate constants are obtained by plotting the pseudo first order rate constant versus surface to volume ratio, using the measured BET surface of the particles. Surprisingly, the BET isotherm gave the same specific surface area for all four size fractions, 5 m²/g. SEM images of the largest and smallest particle fractions revealed that the larger particles have rougher surfaces than the smaller ones, which could explain the unexpectedly high BET surface area of the larger size fractions compared to the smaller ones. If we instead calculate the second order rate constant based on the geometrical surface, the correspondence with theory is better (Table 3 and Fig. 2), indicating that the BET surface area is not an accurate measure of the surface accessible to the oxidant.

The activation energy for the oxidation of the UO_2 pellet by MnO_4^- was determined to be 22.2 kJ/mol. If we think of the pellet as one large particle ($R_p \approx 0.5$ cm) we would expect the activation energ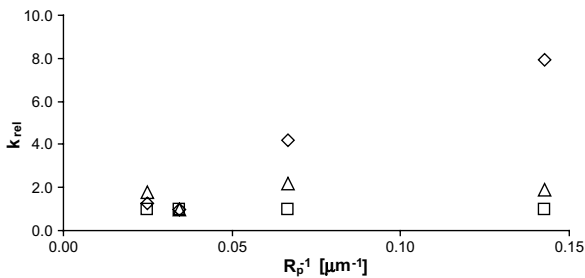y of the pellet to be significantly lower than for the powders (≈ 2.5 kJ/mol), in accordance with Eq. (2) and the trend in our results from the powder experiments. However, since the pellet consists of pressed and sintered UO_2 powder, it could be considered as a cluster of smaller particles and the result is then not that surprising. It should be noted that in terms of collision theory a fuel pellet must be regarded as one single unit and the pre-exponential factor is hence determined by the size of the pellet rather than the grain size.

In Fig. 3 we have plotted the relative measured activation energies for the powders and the pellet (using the grain size of the pellet, $R_p = 2.82$ μm, as reported by the supplier) together with the relative activation energies calculated from Eq. (2). The error bars correspond to the uncertainty in each of the experimentally determined activation energies. As can be seen from the figure the agreement between the powder experiment and the pellet experiment, when treating the pellet as a cluster of small particles, is very good as well as the agreement with theory, considering the uncertainties in the experimental data.

In high burn-up spent nuclear fuel, a decrease in particle size (to a grain size of 1–2 μm in diameter) on the surface of the pellets compared to the fresh fuel has been observed [12]. Hence, we would expect the activation energy to be even higher for the spent fuel than measured for the UO_2 pellet. If the grain size, for example, should decrease to 1 μm diameter, the activation energy would increase to 23.4 kJ/mol. Consequently, because of the high activation energy, the temperature in the deep repository will be a crucial factor in determining the final dissolution rate of the spent fuel.

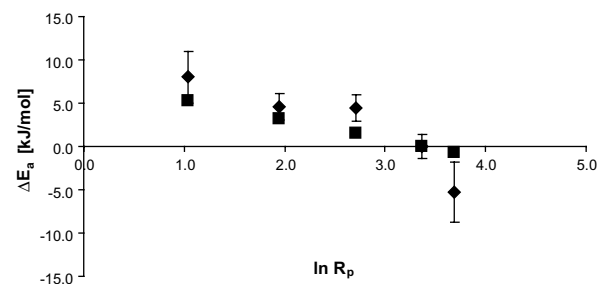Using the linear relationship between the reduction potential and the second order rate constant

Fig. 2. Second order rate constants for the reaction between UO_2 and MnO_4^- plotted versus R_p^{-1} for four size fractions of UO_2 powder. Experimental rate constants, based on BET surface (◇) and geometrical surface (△), respectively, compared with theoretical rate constants (□).

Fig. 3. Experimental (◆) and theoretical (■) relative activation energies for the reaction between UO_2 and MnO_4^- plotted versus ln R_p for four size fractions of UO_2 powder and a UO_2-pellet.

established by Ekeroth and Jonsson [5], the activation energies can be calculated for other oxidants as well. The relationship is based on experiments where no carbonate was added. However, the relative trend should be valid also for systems containing carbonate. For H_2O_2 and O_2 ($E^0 = 0.46$ and -0.15 V respectively [13]), two oxidants believed to be relevant in a future deep repository, the activation energy was calculated to be 24.5 kJ/mol and 36.8 kJ/mol, respectively, for the reaction with a fuel pellet of grain size 5.64 μm.

Some important conclusions can be drawn from this study. We found that the trend in the experimentally determined second order rate constants and activation energies agree quite well with the presented theory (Eqs. (1) and (2)). However, the BET surface cannot always be relied on as an accurate measure of the surface accessible for reaction in a heterogeneous system. Furthermore, the measured activation energy for a UO_2-pellet showed that, in this respect, the pellet is best looked upon as a cluster of smaller particles with diameter equal to the grain size of the pellet. A decrease in grain size due to in-reactor irradiation would increase the activation energy of the spent fuel and slow down the oxidative dissolution process. This effect can however be counteracted by other changes in the surface structure, such as cracking.

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