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Kinetics of decomposition of hydrogen peroxide on the surface of magnetite at high temperature

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ABSTRACT

A novel electrochemical method was employed to accurately measure the kinetics of H_2O_2 decomposition on the surface of magnetite at elevated temperatures and pressures. Electrochemical impedance spectroscopy was used to probe the decay of H_2O_2 concentration by tracking the charge transfer resistance on the surface of a platinum electrode. It was found that the decomposition kinetics follow a first-order rate law with respect to H_2O_2 concentration and vary from 8.1×10^{-4} to 7.9×10^{-2} min^{-1} when the temperature increases from 298 to 473 K (for a 0.2 g L^{-1} magnetite suspension). The mean calculated activation energy of 30 ± 1 kJ mol^{-1} showed that H_2O_2 decomposition on the surface of magnetite particles is a chemically controlled process.

1. Introduction

H_2O_2 is an oxidizing molecular product formed in the heat transport system of nuclear reactors during the radiolysis of water [1–3]. The presence of such a reactive species might significantly affect nuclear reactor water chemistry and the corrosion mechanisms of any structural materials [1,4,5]. Since metal and metal oxide surfaces can catalyze the decomposition of H_2O_2, it is important to understand their interaction at reactor operating conditions in order to accurately monitor the water chemistry and integrity of structural materials [6–8].

Heterogeneous decomposition of H_2O_2 and the catalytic effects of many oxides have been studied extensively in recent publications. H_2O_2 (and its associated compounds) play an important role in a number of industrial applications such as in nuclear power plants, supercritical fluid oxidation, and environmental remediation [2,7,9–16]. The measurement and evaluation of the kinetic rate constants, reaction orders, activation energies and mechanisms of H_2O_2 decomposition have been the focus in these recent studies. In general, one can conclude from these studies that the catalytic decomposition of hydrogen peroxide follows a first-order kinetic rate law with respect to H_2O_2 concentration. It has also been shown that the reaction rate constant is a temperature dependent variable and that the presence of oxide surfaces significantly lowers the measured activation energies of H_2O_2 decomposition. For instance, Lousada and Jonsson investigated the kinetics of H_2O_2 decomposition on the surface of ZrO_2 from 298 to 353 K [17]. They obtained first-order and second-order rate constants at 298 K of 6.15×10^{-5} s^{-1} and 2.39×10^{-10} ms^{-1}, respectively. The calculated activation energy in their study was $E_a = 33 \pm 1.0$ kJ mol^{-1} which is much smaller than direct H_2O_2 decomposition through O–O bond cleavage ($E_a = 210$ kJ mol^{-1}). In another study, Hiroki and LaVerne evaluated the catalytic H_2O_2 decomposition behavior of SiO_2, Al_2O_3, TiO_2, CeO_2 and ZrO_2 up to 398 K. They found first-order kinetics and nearly the same activation energy for all of these oxides: $E_a = 42 \pm 5.0$ kJ mol^{-1} [7].

Iron oxide deposits, which usually form due to particulate fouling by corrosion products, can deposit on heat transfer surfaces in nuclear reactors [18–21]. Amongst the wide range of corrosion products that have been characterized in nuclear power plants, iron oxides (Fe_3O_4 in particular) are known to be a major component [22–24]. In this study we focused on magnetite and its catalytic behavior at different temperatures up to 473 K.

To our knowledge the kinetics of H_2O_2 decomposition on the surface of magnetite have not yet been studied at high temperatures and pressures. In addition, most of the previous studies were done at room temperature at acidic pH where Fenton-like reactions are expected to take place [2,3,25–27]. It is likely that the reason that previous studies were not conducted at high temperature is due to the difficulties of employing the standard titration method for peroxide measurement under these conditions.

In the present work we employ a novel approach to study H_2O_2 decomposition on the surface of magnetite particles. Electrochemical impedance spectroscopy (EIS) is employed to monitor the decay of H_2O_2 using a Platinum probe. Therefore, by using an autoclave and the proposed technique, one can overcome the temperature/pressure limitations of the standard titration method. The

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experiments presented herein were conducted up to 473 K and are the second phase of ongoing work aimed at reaching temperature and pressure conditions closer to those of the supercritical point of water. Our previous work presented the novel impedance technique used to measure the rate of peroxide decomposition on magnetite at 298 K [5]. These room temperature results were in excellent agreement with those obtained by the standard titration method. In the present study, we rely largely on impedance data (rather than titration) to measure the H_2O_2 decomposition kinetics at high temperature and pressure. However, the titration method is also employed in some cases to confirm impedance results and to demonstrate that the method developed in our previous work is applicable at high temperature.

2. Experimental

Electrochemical studies of hydrogen peroxide containing systems usually use $NaClO_4$ as the supporting electrolyte since it does not alter the reduction kinetics [28]. The reason for this lies in the fact that the ClO_4^- ion is large enough that it does not adsorb to the electrode surface, thus it cannot pass through the Helmholtz layer. In this work, 0.1 M deaerated $NaClO_4$ solution was used as the supporting electrolyte and the solution was sparged with N_2 gas for at least 15 min prior to the experiments. Nuclear power plant primary coolant pH is adjusted by the addition of LiOH to pH 6.9–7.4 for the pressurized water reactors (PWRs) and pH 10.2–10.8 for the CANDU reactors (CANada Deuterium Uranium) [29]. In this work the solution contained 0.01 M borate ($Na_2B_4O_7$) to provide a good buffer capacity and pH was adjusted to 9.2 by addition of NaOH. Deionized water (18.2 MΩ NANOpure DIamon.3d, Barnstead, USA) was used in the preparation of all the solutions.

All the decomposition kinetics measurements were carried out in the autoclave. In order to avoid any possible contamination, and also to reduce the influence of the metallic parts of the autoclave on the decomposition kinetics, a glass liner was used in the autoclave and other metallic parts were covered with PTFE. Previous studies have used platinum or modified platinum electrodes as a probe for detecting H_2O_2 concentration in the solution [30,31]. However, these were at room temperature and also in the absence of oxide surfaces. Here, a 0.5 mm OD platinum wire was used as a working electrode (as H_2O_2 concentration probe) and a platinum foil (6 cm^2 surface area) served as a counter electrode, along with a Ag/AgCl External Pressure Balanced Reference Electrode (EPBRE) with a double-porous junction. A Princeton Applied Research Versastat 3F potentiostat/galvanostat was used to conduct the EIS experiments. All the single-sin EIS experiments were carried out by potentiostatic polarization at the previously measured open circuit potential (OCP). For instance, for $[H_2O_2] = 10^{-2}$ M, the OCP decreased from ~0.48 V to ~0.33 V (vs. SHE_T) when the temperature increased from 298 to 473 K. Likewise, at constant temperature of 473 K, OCP decreased from ~0.33 V to ~0.23 V (vs. SHE_T) when the concentration of H_2O_2 decreased from 10^{-2} M to 10^{-6} M. SHE_T here stands for the measured potentials vs. SHE at the operating temperature. For details of the conversion of SHE_T to $SHE_{25°C}$ the reader is referred to reference [32]. These measured OCPs were in agreement with the work done by Nickchi and Alfantazi who studied the kinetics of reduction of H_2O_2 on a Pt electrode at temperatures up to 473 K [33]. A perturbation amplitude of 10 mV (peak to peak) was used in the frequency range of 10 kHz to 50 mHz and at a sampling rate of 10 points per decade. The steady-state OCP of the system was obtained when potential changes of no more than 5 mV in 5 min were detected.

The H_2O_2 decomposition kinetics were measured in the presence of magnetite particles (0.2, 0.5 and 1 g L^{-1}) with a size range of ~0.5–10 μm (86 m^2/g) and the initial concentration of $[H_2O_2] = 10^{-2}$ M. In order to investigate the effects of temperature on the kinetic parameters, the measurements were performed at temperatures of 298, 323, 373, 423 and 473 K at the equilibrium pressure of the electrolyte for a given temperature. In all cases the suspension was stirred at an adequate speed to deliver off-bottom suspension of the iron oxide particles. Single-sin EIS experiments were performed on the platinum working electrode at OCP and various time intervals (5 or 10 min) immediately after the autoclave reached the temperature set point. To ensure the accuracy of the peroxide concentration data measured by EIS, solution samples were also taken from the autoclave at random times. This was done by opening a valve and passing a small volume of solution through a filter (to stop particle entrainment to the sampler) and into a stainless steel sampling bomb (100 mL). Tap water was circulated through copper tubing that was coiled around the sampling bomb in order to prevent thermal decomposition of the H_2O_2 remaining in the sample. The solution samples were then filtered again (0.22 μm filter paper) and the concentration of H_2O_2 was measured by permanganate titration, which has a detection limit of $[H_2O_2] = 1 \times 10^{-4}$ M.

3. Results and discussion

3.1. Electrochemical impedance spectroscopy

EIS was employed to measure the rate of H_2O_2 decay at various temperatures and concentrations of magnetite particles. Fig. 1a and b shows typically observed complex plane and bode plots for the Pt probe obtained at 373 K and in the presence of 0.5 g L^{-1} magnetite particles. The initial concentration of H_2O_2 was 10^{-2} M and EIS experiments were carried out as a function of time (10 min intervals). To ensure that the EIS plots were in line with expected values and were representative of the corresponding H_2O_2 concentration at a given reaction time, the impedance results in solutions of fixed H_2O_2 concentration (5×10^{-4}, 5×10^{-3} and 10^{-2} M) without suspended particles are also overlaid in Fig. 1a. It can be seen that the radius of the semi-circular capacitive loop tends to increase with decreasing H_2O_2 concentration. The same experiments were carried out at all temperatures (298–473 K) and different magnetite particle concentrations (0.2, 0.5 and 1 g L^{-1}) and the same trends were observed. For instance, Fig. 2 shows the complex plane and bode plots for the Pt probe from 298 to 473 K at the beginning of the experiments ($t = 0$) and initial H_2O_2 concentration of 10^{-2} M in the magnetite suspension of 0.5 g L^{-1}. The charge transfer resistance has a reverse proportionality to temperature, which is expected as the kinetics of chemical reactions increase with temperature.

The redox chemistry of H_2O_2 in aqueous solution can be shown via reactions (3.1)–(3.3) [28].

$$H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O \quad E^0 = 1.77\ \text{V(vs. SHE)} \tag{3.1}$$

$$O_2 + 2H^+ + 2e^- \leftrightarrow H_2O_2 \quad E^0 = 0.68\ \text{V(vs. SHE)} \tag{3.2}$$

$$HO_2^- + H_2O + 2e^- \leftrightarrow 3OH^- \quad E^0 = 0.87\ \text{V(vs. SHE)} \tag{3.3}$$

The anodic and cathodic half-cell reactions fix an equilibrium potential on the surface of the platinum electrode. For any of these electrochemical processes (Eqs. (3.1)–(3.3)), the dependency of the steady state current density on the charge transfer resistance obtained from EIS can be expressed as follows [34].

Consider a simple oxidation reaction

$$M \rightarrow M^{n+} + ne^- \tag{3.4}$$

The steady faradaic current can be expressed in terms of Tafel kinetics as