

Kinetic aspects of SCWO progress of solid organic substances

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Abstract

The specific surface reaction rates of Breasol coal and styrene–divinylbenzene resin particles in sub and supercritical water with O₂ were investigated in the temperature range of 300–450 °C at 25 MPa by observing the size change using a shadowgraph method. The rates were approximately proportional to the O₂ concentration and non-linearly dependent on the flow rate. The rate obeyed the Arrhenius law at lower temperatures, but became gradually independent on the temperature above 400 °C, which indicated that the overall reaction is controlled by a certain mass transfer process at the higher temperatures. Compared with the case of coal and activated carbon, much smaller amount of O₂ is enough to result in the rapid size decrease rate in the resin particle.

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1. Introduction

In the supercritical water oxidation (SCWO) progress of solid substances, mass transfer processes of oxidants (in some cases, products) and heterogeneous reactions on the solid surface and/or inside the solid play important roles to determine the overall kinetics, whose understanding is necessary for the practical application of SCWO technology. However, kinetic analysis of solid substances is not well documented, because of the difficulty of directly pursuing the reaction progress. Recently, we have succeeded to investigate kinetic behaviour of carbon (activated carbon and graphite) particles under SCWO conditions, using optical shadowgraph method (Sugiyama et al., 2004a), Schlieren photography (Sugiyama et al., 2004b) and X-ray radiography (Fujie et al., 2005). The rate limiting step and the specific surface reaction rate have been studied (Koda et al., 2006). In this paper, we extended the work to more practical targets, i.e. particulate coal and resin. Their kinetic behaviours were investigated by means of shadowgraph photography.

2. Experiments

The schematic description of the reaction cell and flow systems is given in Fig. 1. The details were described previously (Sugiyama et al., 2004a; Koda et al., 2006). Briefly, the experimental system consists of the cylindrical reaction cell perforated in a Hastelloy block equipped with a sample-transfer mechanism, a flow system and optics. Inside the Hastelloy block is holed through vertically a cylinder of 8 mm in diameter and the fluid flows upward. Two other cylindrical holes are perforated at the right angle to the vertical cylinder and also to each other. The each end is equipped with a sapphire window. The Hastelloy block is heated with rod heaters immersed in the block. The cylinder is connected to another cylinder through a ceramic insulator and cooling fins, because of which the temperature of the latter cylinder is kept cool.

A particle of ca. 2 mm radius fabricated from coal (Breasol coal) or polymerized styrene–divinylbenzene resin (mole fraction before polymerization: styrene 0.92 vs divinylbenzene 0.08. Elemental analysis of the synthesized resin: C 92 mass% vs H 8 mass%) was transferred into the cylindrical cell at the observation point at a desired moment from the lower cylinder. The time change of the particle was then

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observed continuously by means of shadowgraph with a CCD video-camera.

3. Results and discussion

Some typical series of shadowgraphs obtained from coal and resin particles are shown in Fig. 2. The mean radii of the particles were measured from the individual images. The radius (R) decreased almost linearly against the elapsed time. The phenomenological reaction rates, dR/dt , were thus obtained from the slope under various conditions, which can be converted to the surface specific rates, q_s ($\text{kg m}^{-2}\text{s}^{-1}$), according to the

following equation:

$$q_s = \rho_p \times (dR/dt),$$

where ρ_p is the particle density. The density adopted is 1.4, 1.1 and 0.75 g cm^{-3} for the coal, resin and activated carbon, respectively.

Fig. 3 shows that the rate is approximately proportional to the O_2 concentration at 400°C , whereas it tends to saturate with increasing the O_2 concentration at 350°C or 300°C . The latter behaviour may be caused by the solubility limit of O_2 (about 2.8 mass% at 350°C : 1.9 mass% at 300°C) (Japas and Franck, 1985) in subcritical water. Fig. 4 shows the effect of the flow rate. The reaction rate increases very rapidly with increasing the flow rate and tends to become only weakly dependent. The overall dependency is understood to be due to the mass transfer limitation from the bulk, and indeed a similar dependency was found in the previous study of activated carbon (Sugiyama et al., 2004a), where the global reaction at higher temperatures is limited by the O_2 transfer from the bulk to the activated carbon.

The reaction rates are plotted against the reciprocal reaction temperature ($1/T$) in Fig. 5, where the rates for the activated carbon particle are reproduced from the previous work (Koda et al., 2006). It is clearly seen that the rates of the resin are much larger than those of coal and/or activated carbon. The non-linear Arrhenius plot in the activated carbon had been concluded to correspond to the change of the rate determining step from the heterogeneous reaction to the O_2 mass transfer at the higher temperatures (Koda et al., 2006). The very similar behaviours in the temperature effect among the coal, resin and the activated carbon strongly suggest the similar change

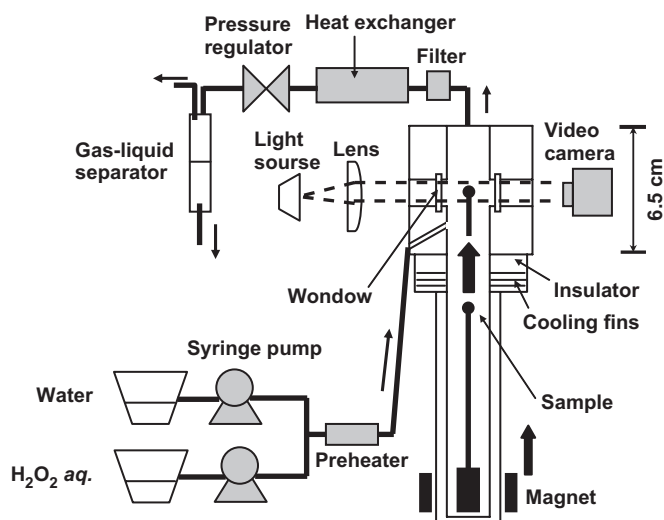


Fig. 1. Experimental set-up.

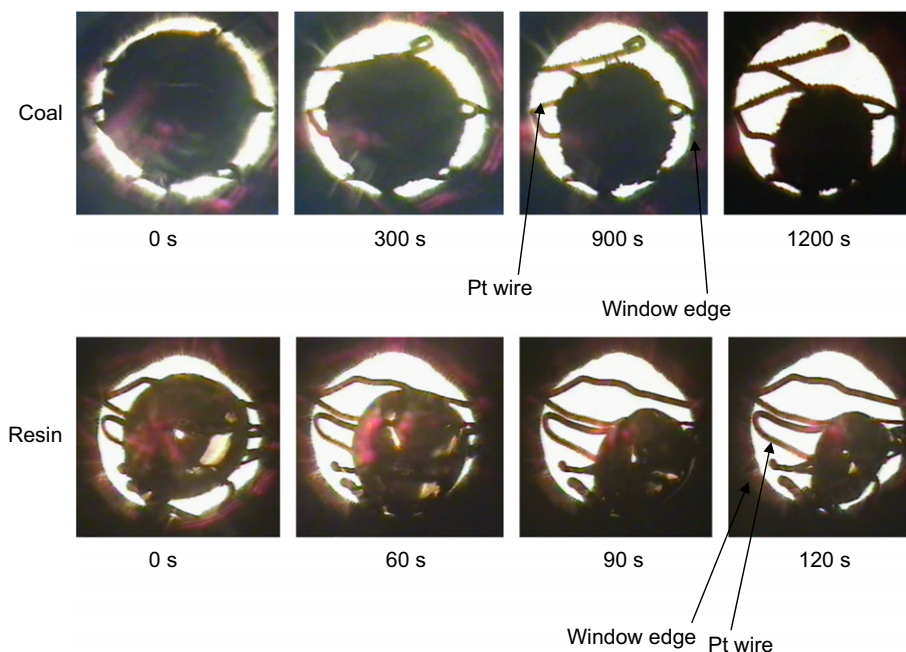


Fig. 2. Time change of coal and resin particle. Conditions: temperature, 350°C ; pressure, 25 MPa; flow rate, $1.67 \times 10^{-2} \text{ cm}^3 \text{ s}^{-1}$; O_2 concentration, 3.6 (coal) or 1.8 mass% (resin).

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