

Reaction kinetics analysis of the dechlorination process of PCBs by sodium dispersion process

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Abstract

The observation experiments of the dechlorination process of PCB with sodium dispersion (SD) single particle have been carried out using a laboratory scale reactor. The dechlorination reaction occurred near the surface of the particle. The particle diameter of SD particle became smaller and the layer of product became thick with the progress of the reaction. The dechlorination reaction can be expressed by the shrinking core model (SCM). The experiment of PCBs with dense SD particles was carried out, and the formulation of the reaction rate was developed. The experiment of PCBs and dense SD particles was carried out, and the formulation of the reaction rate was developed. The temperature of the feasible reactor was simulated during dechlorination process. The calculation results from the formulation excellently correspond to the experiment values. The temperature of the feasible reactor was simulated during dechlorination process. The simulation results showed the maximum temperature of the feasible reactor rose with the decrease of the diameter of the SD particles. The SD particles diameter of about 10 μm that can be made technologically easily was considered to be an optimum condition.

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1. Introduction

Polychlorinated biphenyls (PCBs) were used in a wide range of industrial applications, such as oil in transformer, dielectrics in capacitors, plasticizers, carbon-less copy paper, and dyes. About one million tons of PCBs were produced all over the world between the 1930s and 1970s (United Nations Environment Programme, 2002). The effects of PCBs on health and environment, such as introducing PCBs through the food chain and causing serious health problems in humans, was gradually known after which their manufacture was almost prohibited in the 1970s (Willmann, 1977; Finlayson, 1984). Concerned over the impact of PCBs on the environment and their persistence, the Japanese Ministry of International Trade and Industry

enforced the industries to stop the production of PCBs and to begin to collect PCBs for destruction after 1972.

In Japan after incineration of 5500 ton of liquid PCBs at very high temperature by Kaneka Corporation at Takasago Plant 12 years ago, destruction processing of PCBs has not progressed yet, except for the chemical processing procedures by some companies since 1999. Then, the committee for examining the proper processing techniques and technologies of PCBs such as high-temperature incineration, chemical and photochemical dechlorination, and catalytic dechlorination in both gas and liquid phase were established by the Ministry of Environment in 1997, and the guidelines about the processing methods were produced in the argument from a scientific and technical viewpoint in 2000.

Among those methods, the sodium dispersion (SD) process is one of the most attractive methods, the advantage of which are: (1) effective dechlorination is possible at low-temperature

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under atmospheric pressure; (2) process cost is low because of the simple reaction principle; (3) batch process can easily be employed for the highly active reaction of the sodium metal as well; and (4) no toxic by-products (i.e., biphenyl, phenylcyclohexadiene, and phenylcyclohexene) are formed (Ariizumi et al., 1997). This method is inexpensive, technically flexible, and dechlorination of various stable PCBs readily takes place, but no studies have been carried out in the environment impact by evaporation during reacting process when the reaction temperature reaches a high level for exothermal reaction which is the fundamental requirements to the selection of a proper processing procedure. It is indispensable to confirm the safety of the SD process and the optimal operating conditions as fundamentally experimental study before recognized in public as a proper process for destructing the PCBs. The experiments in a laboratory scale can give much information for clarifying the reaction phenomena, discovering the key factors affecting the process to control the reaction stably.

In the present work, the observation experiment of reactive process of PCBs and SD single particle was carried out with a reactor of laboratory scale, and the reaction process of PCBs with SD particle was analyzed using the regular kinetic model. The experiment of PCBs and dense SD particles was carried out, and the formulation of the reaction rate was developed. The temperature of the feasible reactor was simulated during dechlorination process.

2. Experiments

2.1. Materials

The biphenyl tetrachloride (KC400) most preserved in Japan was used in the experiments. Electric insulation oil (Idemitsu Transformer Oil) was used as the solvent. The SD particles had a mean diameter of $7.5\ \mu\text{m}(\pm 5\%)$ that had been micronized from the metal sodium of 99.6% in the purity were used as SD.

2.2. Single particle experiment

The experimental apparatus, as shown in Fig. 1, consisted of a CCD camera, C mount, an optical microscope, a reactor, a heater, and a thermocouple. The reaction was performed in a petri laboratory dish (as a reactor) of 30 mm of diameter, and 15 mm of height. In order to let light pass from the bottom, two Ribbon heaters positioned under the reactor were used to form an opening of 2 mm. The thermocouple was the K-type thermocouple. The CCD camera was connected with the optical microscope by the C mount as well as with a personal computer to observe simultaneously the reaction process and record the pictures.

In the experiment, PCBs concentration was set for 10 and 30 wt% at normal pressure, and reaction temperatures under each PCBs concentration were 60, 80, 100, 120, 140, and 160°C , which were same as the processing conditions of the actual SD processing method (Ariizumi et al., 1997). Moreover, during the experiment, the N_2 gas of the experiment equipment is circulated. Prior to the experiment process, both PCBs and

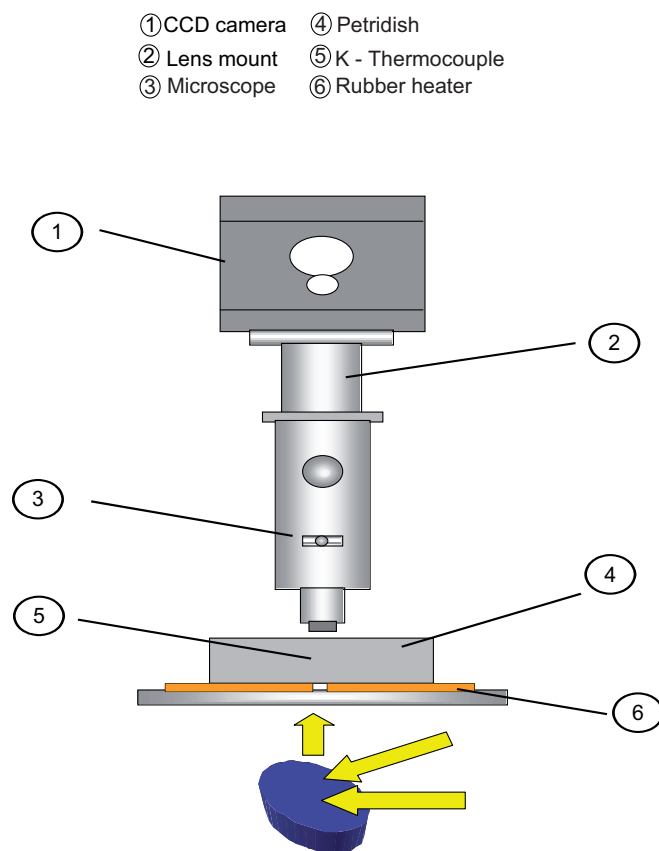


Fig. 1. Experimental apparatus of single particle experiment.

SD were diluted with electric insulation oil. A 3 ml of PCBs with the oil was put into the reactor vessel first and then 0.05 ml of SD into the petri laboratory dish using the micropipette continuously at room temperature. After adjusting the focus of the optical microscope to cover a single SD particle immediately, the heater was operated to heat the reactor to the required temperature. Meanwhile, a change of the diameter of SD single particle with time was taken with the CCD camera.

In this experiment, in order to take the pictures of a change of the SD single particle diameter during the dechlorination process, the experiment process was different with the process of the actual SD processing method. Since SD particle was moving by speed in the process of the actual SD processing method by this research, a change of the particle diameter of the same particle during the dechlorination process cannot be took. Therefore, if this experiment process compared with the process of the actual SD processing method, it had not temperature rising to reaction temperature and had not been stirred, so the reaction advancing in a little late state by this process. In next experiment, the process was same as those of actual SD processing method in a laboratory scale.

2.3. SD dense experiment

The experimental apparatus was shown in Fig. 2. The experiment conditions were same as above. Prior to the experiment

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