



Kinetic analysis of the mixture effect in supercritical water oxidation of ammonia/methanol



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ABSTRACT

Reaction kinetics of supercritical water oxidation (SCWO) of ammonia/methanol mixture was investigated at 530 °C, 25 MPa, and $[\text{NH}_3]_0 = 2.9\text{--}3.0$ mmol/L, both experimentally and computationally. Ammonia conversion increased with an increase in the initial methanol concentration. Ammonia oxidation was retarded after complete oxidation of methanol. The major product from ammonia oxidation was N_2O . Methanol decomposition and CO oxidation were accelerated in the ammonia/methanol mixture under the conditions used. Calculations using an elementary reaction model show that ammonia and methanol mutually promote their oxidation through radical intermediates. The mixture effect in the SCWO of ammonia/methanol can be explained by a radical chain mechanism in which ammonia and methanol share the radicals generated and promote mutual oxidation reactions. The ammonia oxidation cycle initiated by methanol co-oxidation was maintained by nitrogen-containing species even after methanol had been completely oxidized.

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1. Introduction

Supercritical water oxidation (SCWO) is recognized as a technique for the destruction of hazardous organic waste. Since the reactions in this method proceed in water, SCWO can be applied to the treatment of waste streams containing a high percentage of water. Studies on using SCWO for detoxifying organic waste streams such as landfill leachate, coking wastewater, and sewage sludge have been well documented [1–3]. These streams generally contain a mixture of nitrogenous organic compounds. There are numerous reports in the literature on using SCWO for the treatment of not only industrial waste streams [1,2] but also model compounds; alcohols [4,5], phenol [6], ammonia [7], urea [8], methylamine [9,10], nitrobenzene [11], and 2,4-dinitrophenol [12].

Based on previous studies, the destruction of ammonia is the rate-determining step in the SCWO of wastewater [13–15]. Some reports [14,16,17] have suggested that ammonia is a recalcitrant species in typical conditions used during SCWO (400–600 °C, 24–5 MPa). For example, Segond et al. reported that only 29% ammonia had converted at 600 °C, and 24.5 MPa in 23.1 s [16].

Some researchers have used alcohols such as methanol [18], ethanol [17,19,20], and 2-propanol [21–23] in the SCWO process, confirming that the conversion of ammonia could be enhanced by controlling coexisting materials. Kinetic experiments on the effect of alcohol on ammonia oxidation have showed that the reaction mechanism of this process is similar to gas-phase combustion chemistry. Oe et al. investigated the effect of methanol on ammonia conversion and the product yields under the typical operating conditions of a commercial plant at 560–620 °C and 25 MPa, varying the methanol-ammonia feed ratio from zero to 20 [18]. When the methanol-ammonia feed ratio was more than two, the conversion of ammonia to N_2O increased by about four times compared to the reference case where no methanol was added. Furthermore, H_yNO_x (mainly HNO_3) started forming when the initial methanol concentration was thrice that of ammonia at 560–620 °C for 60 s. Ploeger et al. examined the SCWO of ammonia/ethanol at 655–705 °C experimentally. They have reported that at 2.5 s residence time and in the presence of stoichiometric oxygen, the conversion of ammonia increased from 20 to 65% when a molar equivalent of ethanol was added at 700 °C and 246 bar [19]. Pure ammonia oxidation yielded only 3% of N_2O . However, a slightly better 11% yield of N_2O was obtained during the co-oxidation with ethanol at $T = 700$ °C for 3.5 s, when the initial ammonia and oxygen concentration was fixed. According to simulations based on a

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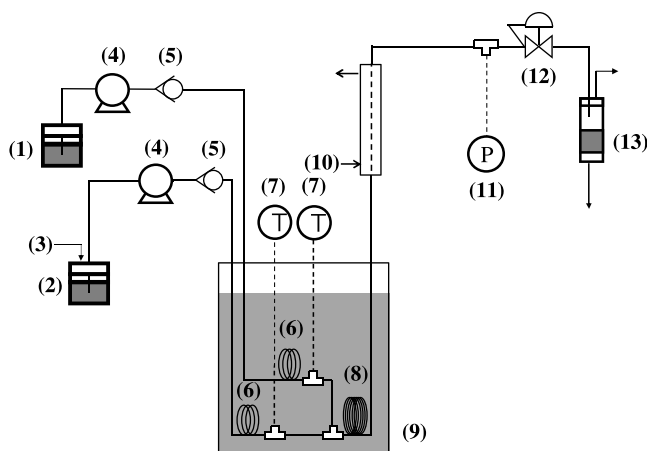


Fig. 1. Experimental apparatus: (1) aqueous $\text{NH}_3/\text{CH}_3\text{OH}$ solution feed tank, (2) aqueous H_2O_2 solution feed tank, (3) He gas, (4) pump, (5) check valve, (6) preheating line, (7) thermocouple, (8) tubular reactor, (9) sand bath, (10) cooling water, (11) pressure gauge, (12) back pressure regulator, (13) gas-liquid separator.

detailed chemical kinetics model of ammonia/ethanol co-oxidation [20], ammonia oxidation is initiated by the reaction with OH radicals, and a high HO_2 radical concentration drives more of the ammonia oxidation flux through the $\text{NH}_2 + \text{NO}_x$ submechanism, which finally leads to N_2O formation. However, a further understanding of the reaction mechanism especially at the initial stages of ammonia decomposition and N_2O formation is required to improve SCWO techniques for processing N-containing waste streams.

Radicals concerned with ammonia oxidation are considered to be produced by alcohol co-oxidation. Therefore, the radical chain reaction mechanism and the oxidation behavior may be altered by temporary changes in the behavior of alcohol oxidation. There have been no investigations reported so far on this crucial relationship. In addition, the initial alcohol concentration can be one of the key parameters influencing the ammonia oxidation rate. Ploeger et al. [19] have reported a study on the effect of changing the initial ethanol concentration in ammonia/ethanol SCWO at a fixed stoichiometric oxygen concentration. In their experiments, since the initial oxygen concentration changed with the initial alcohol concentration, the effects of the initial alcohol concentration are unclear. No other studies have examined these two effects from a kinetics perspective.

The objective of this study is to clarify the effects of methanol co-oxidation on SCWO of ammonia in detail. Kinetics of methanol and ammonia co-oxidation on the conversion and product distribution are investigated. Simulations based on a detailed chemical kinetic model (DCKM) to elucidate the reaction mechanisms involving radicals are performed.

2. Experimental

2.1. Apparatus and experimental procedures

The experimental apparatus used in this study is shown in Fig. 1. The SCWO experiments were conducted in an isothermal, isobaric tubular reactor held at a temperature of 530°C , and a pressure of 25 MPa. Aqueous solutions of the ammonia/methanol mixture and hydrogen peroxide were separately fed into coiled preheating lines using two HPLC pumps (JASCO Corp., PU-980 and PU-2080). The preheating line for the ammonia/alcohol solution was made of a SUS 316 tube (3 m, 1/16 inch o.d., 1.00 mm i.d.), and that for the $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixture was made of a SUS 316 tube (3 m, 1/8 inch o.d., 2.17 mm i.d.). Oxygen was obtained by complete decomposition of an aqueous hydrogen peroxide solution fed into the preheating

line. After the preheating line, each flow temperature value was measured with a sheathed thermocouple (Sakaguchi Denki Co.). The two streams were mixed in a low dead volume tee made of Inconel 625 Ni alloy (Sugiyama Shouji, WF-1/16TTTF-0.5-INC625). The reactor, made of Hastelloy C-276 Ni alloy (1/16 inch o.d. and 0.80 mm i.d.), was immersed in an isothermal fluidized-bed sand bath. The residence time was controlled by the flow rate of the HPLC pumps and the reactor length. The exit stream was fed into a heat exchanger, and then cooled by external cooling water to terminate the reaction. The stream was depressurized to atmospheric pressure with a backpressure regulator (JASCO Corp., BP-2080-M Plus). The exit flow was separated into gaseous and aqueous streams in a gas-liquid separator. The gaseous products (N_2O , CO, and CO_2) were analyzed using a gas chromatograph equipped with a thermal conductivity detector (Shimadzu Corp., GC-8A) and a Shincarbon ST 50/80 column (Shinwa Chemical Industries Ltd.). The gas flow rate was determined by measuring the volume of gas collected in a gas bag for a fixed time. The amount of CO and N_2O in the liquid effluent was calculated using Henry's law at 20°C and atmospheric pressure. The concentration of ammonium ions in the liquid effluent was determined by ion chromatography (JASCO Corp., PU-980 series) equipped with an electric conductivity detector (Showa Denko, CD-5) and a Y-521 (Showa Denko) column. The methanol concentration in the effluent was analyzed using a gas chromatograph equipped with a flame ionization detector (Shimadzu Corp., GC-14B) and a Porapak Q glass column. In addition, the concentration of inorganic carbons in the effluent was analyzed using a total organic carbon analyzer (Shimadzu Corp., TOC-5000A). The liquid sample at each run was sampled three times and each ammonia concentration was analyzed by Ion Chromatography. The arithmetic mean of three values was used. The balance of nitrogen and carbon in the experimental data shown in this study are 0.98–1.04 and 0.90–1.10.

2.2. Materials

The reactant solution was prepared by dissolving methanol (purity > 99.8%, purchased from Wako Pure Chemical Industries, Ltd.), and ammonia (28–30%, purchased from Kanto Chemical Co., Inc.) into water. The water used in this study was distilled in a distillation apparatus, which was bubbled with helium gas for more than 30 min prior to use. The $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ solution was prepared using 30.0–35.5 wt.% $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ stock solutions (purchased from Wako Pure Chemical Industries, Ltd.) to set the initial oxygen concentrations to be at least 3.1 times greater than the stoichiometric oxygen concentration so that there will be excess oxygen even after the complete oxidation. All the experimental conditions are displayed in Table 1. The initial ammonia concentrations were 3.0 mmol/L, and the initial methanol concentrations were 1.5–9.3 mmol/L at 530°C and 25 MPa.

2.3. Elementary reaction models

Previous studies [20,24–33] have reported models with detailed chemical kinetic mechanisms for SCWO. Many of these reports have suggested that SCWO proceeds via radical chain reactions very similar to those in gas-phase combustion chemistry under the typical operating conditions. In this study an elementary reaction model was developed by combining the two reported models of methylamine oxidation [29] and ethanol/methanol [27] oxidation in supercritical water. All the calculations were performed using CHEMKIN 10131 [34].

In this simulation, the rate constants for a reverse reaction were calculated using the equilibrium constants in concentration terms, which depend on the temperature and the compressibility factor (Z), when the difference between the stoichiometric coefficients

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