The Behavior of Nitrogen Oxides in the N_2H_4–NO–O_2 Reaction

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INTRODUCTION

It has been discovered that NH_3 selectively reduces NO in the presence of a large excess of O_2 over the temperature range of 800 to 1,050°C (Lyon, 1976; Lyon and Benn, 1979). It has also been found that H_2O_2 promotes the NH_3–NO reaction and initiates it at about 500°C (Azuhata et al., 1981, 1982). It is generally accepted that the selective reduction of NO with NH_3 is attributed to the high reactivity of NO with NH_2 and NH radicals, produced during the decomposition of NH_3, and the production of these radicals may be the key technology to reduce NO. Based on this philosophy, much effort has been devoted to finding more effective reducing agents than NH_3 and/or additives that would promote the NH_3-NO reaction for the purpose of developing an NO*x* removal process from a combustion exhaust gas.

The main objective of this work was to determine if an ammonia derivative, N_2H_4, could reduce NO in the presence of a large excess of oxygen. While a significant number of experiments already has been performed on the decomposition of N_2H_4 (Diesen, 1963; Michel el at., 1965; Meyer et al., 1969; Gehring et al., 1979), little information is available to access the applicability of N_2H_4 to an NO reduction process.

EXPERIMENTAL PROCEDURE

The experimental equipment and procedure were basically the same as those previously employed to study the reaction of NH_3-NO-H_2O_2 (Azuhata et al., 1982). The main change to the procedure in the present work was that, instead of H_2O_2, a water solution of N_2H_4 was sprayed to fine droplets by a carrier stream of N_2. The sprayed liquid N_2H_4 was vaporized at 120°C and then injected into an electrically heated quartz tube reactor 1.3 m long and 15, 20, and 40 mm I.D.

The flow rate of each reactant was measured with calibrated rotameters and the total flow rate was set at 100 mL/s (at 0°C and at atmospheric pressure). The content of N_2H_4 in a gas mixture was controlled by varying the concentration of N_2H_4 solution, and checked by the iodometric titration of hydrazinium sulfate, which was obtained by bubbling the sample gas through a dilute sulfuric acid. A Yanagimoto ECL 308 chemiluminescence NO/NO*x* analyzer was used to monitor NO and NO_2. The composition of reactant mixture was 0–1,000 ppm N_2H_4, 0–200 ppm NO, 0–15% O_2, and N_2 as carrier.

EXPERIMENTAL RESULTS AND DISCUSSION

The influence of the reaction temperature on the N_2H_4–NO reaction was studied with and without O_2. Figure 1 shows the relation between reaction temperature and the concentration change of NO, NO_2, and NO*x* (NO + NO_2). The decrease in NO was observed above 500°C, in the absence of O_2. This result was easily predictable based on the kinetic data of the thermal decomposition of N_2H_4 (Eberstein and Glassman, 1965), and NO was thought to be reduced to N_2 and H_2O by N_2H_4.

In contrast, the presence of O_2 prohibited the reduction of NO*x*.

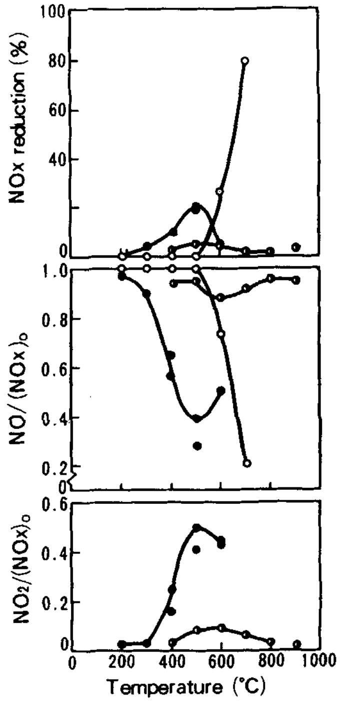

Figure 1. Variations of NO*x* reduction, NO, and NO_2 with reaction temperature in the N_2H_4—NO—O_2 reaction. Gas mixtures: 200 ppm N_2H_4, 200 ppm NO*x* (mostly NO but 0-5 ppm NO_2 as impurity), 0 ~ 15% O_2, balance N_2. ○: O_2 absent; ◐: 3% O_2; ●: 15% O_2.

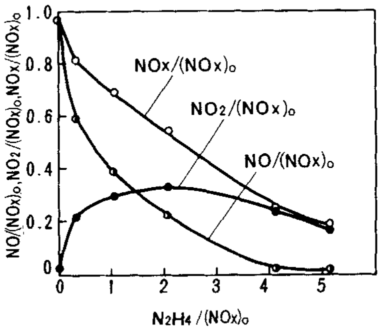

Figure 2. Relation between variations of NO, NO_2, and NO*x* and initial molar ratio of N_2H_4 with NO*x*. Gas mixtures: 0 ~ 1,020 ppm N_2H_4, 200 ppm NO*x* (195 ppm NO and 5 ppm NO_2), 15% O_2, balance N_2. Temp., 500°C; reaction time, 0.4 s.

When 3% O_2 was added to the mixture of N_2H_4 and NO, only a slight change in NO and NO_2 was observed. By increasing the O_2 concentration, the characteristic of the N_2H_4–NO–O_2 reaction became clearer. Ther marked result was the appearance of a large amount of NO_2. Despite the large decrease in NO, NO*x* reduction was very low because of the formation of NO_2. The NO_2 formation showed a large dependence on the O_2 concentration. About five times as much NO_2 was observed in the experiment with the 15% O_2 present as in that with 3% O_2.

If NH_2 of NH radicals were to be produced in the N_2H_4–NO–O_2 reaction, a part of NO would have to be converted to N_2. NH_2 was already proved to be highly reactive with NO, and the reduction of NO with NH_3 was well explained by assuming that NH_2 produced from NH_3 would react with NO in the presence of a large

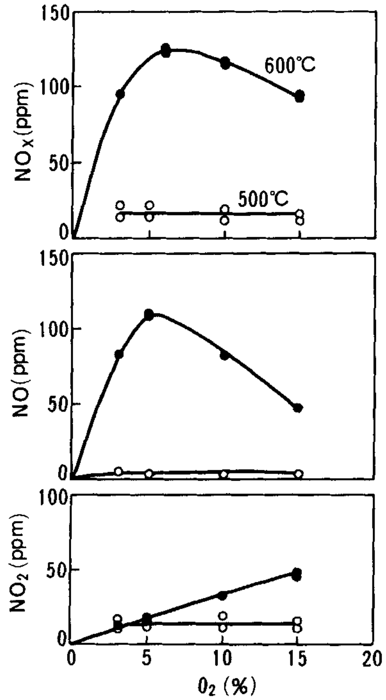

Figure 3. Formation of NO and NO_2 in the N_2H_4—O_2 reaction. Gas mixtures: 1,000 ppm N_2H_4, 3–5% O_2 balance N_2. Temp., 500 and 600°C; reaction time, 0.4 s.

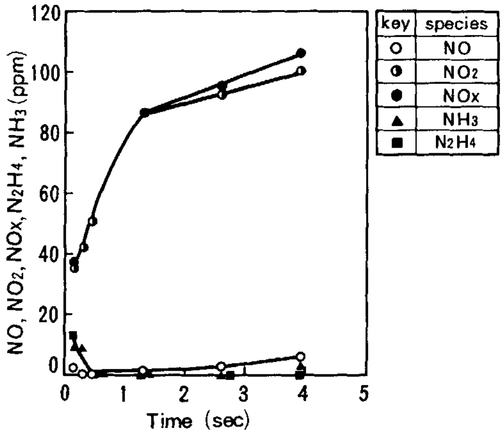

Figure 4. Variations of reactants with time. Gas mixture: 500 ppm N_2H_4, 100 ppm NO*x* (95 ppm NO and 5 ppm NO_2), 15% O_2, balance N_2. Temp., 500°C.

excess of O_2 (Lyon and Benn, 1978; Azuhata et al., 1981). Therefore, the oxidation of N_2H_4 with O_2 is thought to produce only a little amount of NH_2 or some intermediates that would react more rapidly with NH_2 than NO.

Figure 2 shows the influence of initial molar ratio of N_2H_4 to NO*x* on the concentration change of nitrogen oxides. Experiments were conducted at 500°C with 15% O_2 present. The increase in N_2H_4 caused the decrease in NO*x* and NO, and the NO_2 produced exhibited a weak dependence on N_2H_4.

In previous papers, little has been mentioned about the formation of NO_2 or about the reaction mechanism that would predict NO^2 formation. There are three plausible reaction pathways that will predict the NO_2 formation. The first possibility is the NO–O_2 reaction. But this reaction can be ruled out, because it was experimentally verified that the direct oxidation of NO with O_2 did not take place under the experimental conditions of this study. The second possibility is the oxidation of N_2H_4 with O_2, and the third is the oxidation of NO with some intermediates produced from the oxidation of N_2H_4 with O_2.

In order to confirm the relative importance of these two possible pathways, NO and NO_2 produced in the N_2H_4–O_2 reaction were measured. Figure 3 shows the formation of NO and NO_2 obtained when mixtures of 1,000 ppm N_2H_4, 0–15% O_2, and N_2 as carrier were heated to 500 to 600°C. Both NO and NO_2 were detected due to the oxidation of N_2H_4 with O_2. A peak NO was observed around 5% O_2, and NO_2 increased proportionally with O_2, although the sum of NO and NO_2 showed only a slight dependence on O_2. The experimental results in Figure 3 indicated that N_2H_4 was converted to NO_2, but the amount of NO_2 produced was 5% of N_2H_4 at most at 600°C and below 2% at 500°C. These values were far less than those obtained in the reaction of N_2H_4–NO–O_2 shown in Figures 1 and 2. These experimental results would support the assumption that N_2H_4 cannot be the main source of NO_2, and NO_2 must be chiefly produced from NO.

Figure 4 shows the variations of N_2H_4, NO, NO_2, and NH_3 with the reaction time. NO disappeared very rapidly, as did N_2H_4. A trace of NH_3, which was the product of N_2H_4 decomposition, was observed within 0.2 s. In contrast to these reactants, the formation of NO_2 occurred very slowly and continued for more than 1 s in the region where no N_2H_4, NH_3, and NO could be detected.

These results suggest the assumption that the NO_2 formation in the N_2H_4–NO–O_2 reaction takes place in two distinct steps. The first rapid reaction of N_2H_4 with NO proceeds in the presence of O_2 and yields a relatively stable species, which forms NO_2. This reaction is followed by a slower reaction, which produced NO_2.

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