N_2O decomposition using an electric-field-assisted catalysis at low temperatures

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Significance and Relevance

We applied a novel catalytic system, an electric field assisted catalytic system, to nitrous oxide (N_2O) removal, demonstrating that N_2O decomposed into N_2 and O_2 efficiently on the electric field applied Rh catalyst, even at low temperatures below 473 K and in the presence of excess oxygen and water vapour. The reaction mechanism on the catalyst applied with the electric field was investigated using kinetics and various characterisations, which revealed that surface oxygen on the catalyst contributes to N_2O decomposition.

Preferred and 2nd choice for the topic: Air cleaning and combustion and *Automotive and stationary emission control*
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Introduction and Motivations

N_2O is a greenhouse gas that is about 310 times more effective than CO_2 and is also ozone-depleting, so the development of efficient technologies to mitigate its emissions from various sectors, including agriculture, industry, and transportation. N_2O decomposition using heterogeneous catalysts is one of the most promising methods[1], but it is not yet very versatile because it requires high reaction temperatures. Therefore, we focused on a novel catalytic system, an electric-field-assisted catalytic system, and aimed to achieve N_2O decomposition at lower temperatures[2].

Materials and Methods

We prepared ceria-zirconia ($Ce_{0.7}Zr_{0.3}O_2$) for the catalyst support. Preparation was conducted using a citric acid complex method with aqueous solutions of $Ce(NO_3)_3{\cdot}6H_2O$ and $ZrO(NO_3)_2{\cdot}2H_2O$, with excess amounts of citric acid and ethylene glycol. The molar ratio of metal: citric acid: ethylene glycol was 1: 3: 3. After the obtained solution was dried on a hot plate with stirring. The obtained powder was calcined in air at 1123 K for 10 h. Rh species were loaded on $Ce_{0.7}Zr_{0.3}O_2$ using an impregnation method. A slurry was made by adding a powdered $Ce_{0.7}Zr_{0.3}O_2$ to a solution of $Rh(NO_3)_2$. Then, it was dried at 393 K for 20 h and was calcined in air at 823 K for 3 h.

Catalytic activity tests were conducted in a fixed flow-type quartz reactor at atmospheric pressure. An electric field (EF) was applied using a power supply *via* stainless steel electrodes, contacting the catalyst-bed on the upper and lower sides. A direct current of 6 mA was applied to the catalyst-bed. During this activity test applying the EF, the catalyst-bed temperature was measured directly with a thermocouple to verify the effects on the catalytic activity of Joule heating by the applied direct current. Response voltage was measured using a digital phosphor oscilloscope (TDS 2001C with a voltage probe P6015A; Tektronix Inc.). 100 or 200 mg of catalyst (sieve to 250–500 µm mesh) was placed in a quartz tube. Reactant gases were a mixture comprising 1000 ppm of N_2O, 10%O_2, and 10%H_2O. The total gas flow rate was 100 mL min^{-1}. Also, a thermocouple was set at the bottom of the catalyst bed to measure the actual catalyst bed temperature. The outlet gases were detected using a quadrupole mass spectrometer (Thermostar GSD 350; Pfeiffer Vacuum GmbH).

Results and Discussion

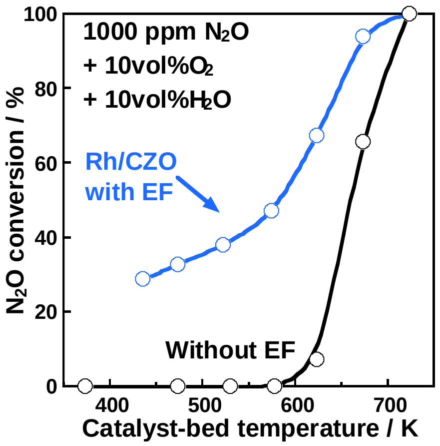
We applied a non-conventional catalytic system, catalytic reactions in an EF, to N_2O decomposition on the 0.5wt%$Rh/Ce_{0.7}Zr_{0.3}O_2$ (Rh/CZO) under 1000 ppm N_2O + 10%O_2 + 10%H_2O. Figure 1 shows the excellent promotion of catalytic activity by application of the electric field, even at low temperatures. To confirm the electronic state of Rh species on CZO both with and without the application of the EF during N_2O decomposition, operando-XAFS measurements were conducted. As a result, the Rh species was found to be Rh_2O_3, indicating that the N_2O decomposition proceeded on Rh_2O_3 surface with or without the EF.

To gain insight into the promotive effect due to the application of the EF on the catalytic activity, we investigated the dependence of the N_2O conversion rate on the partial pressures of N_2O and O_2. Tests were conducted at 423 K with EF and at 638 K without the EF. The dependence on N_2O partial pressure was slightly reduced by the EF; the reaction order was 0.70 (with EF) and 1.10 (without EF), respectively. On the other hand, the dependence on O_2 partial pressure showed a drastic change by the EF application (Figure 2a). On the catalyst without the EF, the N_2O decomposition was hindered by the coexistence of oxygen; −0.51 of reaction order. In contrast, with the electric field, the reaction order was almost zero (−0.06), indicating that N_2O decomposition is not inhibited by coexisting O_2.

Figure 2b-c presents the N_2/O_2 molar ratio in outlet gas during N_2O decomposition under a flow of 1000 ppm N_2O + 10%H_2O with and without the EF. Figure 2b is the result of the catalyst without the EF, revealing that the N_2/O_2 molar ratio exceeded 2 upon the supply of N_2O, with subsequent saturation to a stoichiometric value of 2. This result suggests that N_2O decomposition proceeds through the Langmuir–Hinshelwood (LH) mechanism; the associative desorption of residual oxygen species is slower than the N–O bond cleavage. By contrast, with the electric field, for 20 min after the reaction started, the N_2/O_2 ratio was below 2. This phenomenon demonstrates that N_2O reacts with oxygen species on the surface of Rh/CZO as follows equation:

$$N_2O\,(g) + O^*(\text{surface}) \rightarrow N_2(g) + O_2(g) + {}^*(\text{surface})$$

In conclusion, it was revealed that surface oxygen contributes actively to N_2O decomposition thanks to the application of EF, leading to significant catalytic activity at low temperatures.



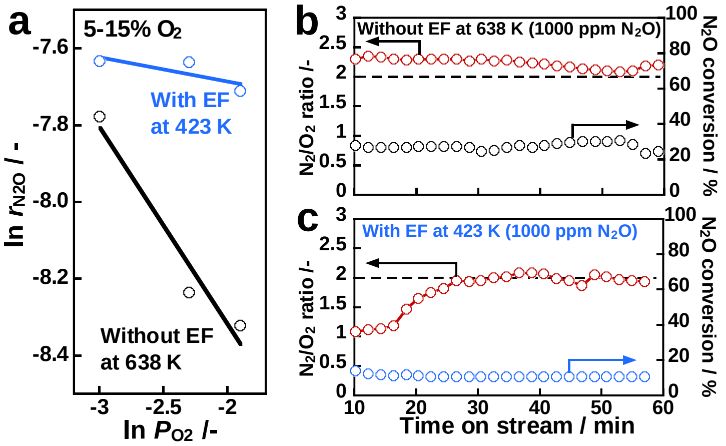


Figure 1. (left) Catalytic activity for N_2O decomposition over 0.5wt%Rh/ $Ce_{0.7}Zr_{0.3}O_2$ with and without the electric field.

Figure 2. (right) (a) Dependence of the decomposition rate of N_2O on the pressure of O_2 and (b) N_2/O_2 molar ratio in out-let gas over 0.5wt%Rh/$Ce_{0.7}Zr_{0.3}O_2$ with and (c) without the electric field.

References

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