—Technical Paper—

Reduction of Nitrogen Oxide Using a Perovskite-type Protonic Conductor $\text{SrZr}_{0.9}\text{Yb}_{0.1}\text{O}_{3-\alpha}$

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A steam electrolysis cell was constructed with a perovskite-type protonic conductor, $\text{SrZr}_{0.9}\text{Yb}_{0.1}\text{O}_{3-\alpha}$, as an electrolyte. The steam electrolysis cell efficiently produced hydrogen in the temperature range from 400 to 600°C. The application of this cell to reduce nitrogen oxide (NO) by the hydrogen was examined. When Pt/Ba/Al₂O₃ catalyst was employed on the cathode, the cell could reduce NO even in O₂-rich atmosphere. The cathode potential of the cell revealed that the reduction of O₂ might be inhibited due to the absorption of NO and O₂ into Ba, and that NO absorbed in Ba might be reduced to N₂ by atomic hydrogen.

Key Words : Protonic Conductor, Nitrogen Oxide, Reduction, Steam Electrolysis

1 Introduction

$\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$, $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\alpha}$, and $\text{SrZr}_{0.9}\text{Yb}_{0.1}\text{O}_{3-\alpha}$ (α ; mole fraction of oxide ion vacancies) with the perovskite-type structure have oxide ion vacancies, and H₂O can be dissolved into the crystal structure according to equation (1),¹⁾

where $\text{V}_{\text{O}}^{\cdot\cdot}$ denotes an oxide ion vacancy, H^+ a proton and $\text{O}_{\text{O}}^{\times}$ an oxide ion at a normal lattice site.^{2, 3)} H₂O dissolved in the perovskite structure forms protons combined with oxide ions at the normal lattice sites by OH bond.⁴⁾ This proton can migrate around semi-stable positions near oxide ions by the hopping conduction mechanism⁵⁾ and may lead to a high ionic conductivity ($\approx 10^{-3}$ (S/cm)) of these materials around 700°C.¹⁾

These materials with a high protonic conductivity have been studied widely for their applications including hydrogen sensors,^{6–10)} SOFCs^{11–15)} and gas reactors.^{16–18)} We have studied on a new device using this protonic conductor in order to reduce nitrogen monoxide (NO),¹⁹⁾ which is one of the most harmful components in exhaust gases of automobiles, because most of nitrogen oxides (NO_x) exist as NO in the exhaust gases. To date, chemical catalysts have been mainly used to reduce NO by hydrocarbons and CO in the exhaust gas. However, this method is not effective under the lean-burn (O₂-rich) condition. Therefore, the development of new methods is required for the effective reduction of NO even under such lean-burn conditions. In this study, we investigate an electrochemical method using a steam electrolysis cell for reducing NO.

Figure 1 shows a schematic diagram of a steam electrolysis cell for reducing NO. The steam electrolysis cell is constructed with a solid protonic conductor as the

electrolyte. Water vapor is electrochemically oxidized on the anode and the protons produced are transported through the electrolyte to the cathode. At the cathode, protons are first reduced to atomic hydrogen, and then hydrogen gases are produced. Therefore, in this cell, it is expected that NO will be reduced not only electrochemically but also chemically. In this system, water vapor in the exhaust gases can be used as a water source for the anode. Therefore, this cell can be a simple and effective device for NO reduction in exhaust gases.

The following reactions may be relevant in such kinds of cells:

The electrochemical reactions between NO and proton may be written as equations (2)~(4). The electrochemical reaction between O₂ and proton may be written as equation (5), which competes with reactions (2)~(4).

Fig. 1 Schematic diagram of a steam electrolysis cell for the reduction of nitrogen oxide.

When an electrocatalyst based on Ba, capable to absorb NO, is set on the cathode of the cell, the related electrochemical reaction may be written as equation (6).

Figure 2 shows the temperature dependence of the standard potential of each electrochemical reaction versus reversible hydrogen potential (RHE). Because the reduction reactions with higher standard potentials usually proceed first, it is expected that NO will be reduced easier than O₂ according to equations (2) and (3).

2 Experimental

Figure 3 shows a cross section of the experimental apparatus. A closed one-end tube of sintered SrZr_{0.9}Yb_{0.1}O_{3-α}²⁰⁾ (supplied from TYK corp.) was used as the protonic conductor. This protonic conductor is chemically more stable than other protonic conductors based on SrCeO₃ and BaCeO₃ in an atmosphere containing CO₂,²¹⁾ which is one of the components in the exhaust gas. Platinum for electrodes was plated on both sides of the electrolyte by an electroless plating method. The areas of the anode and the cathode were 6 cm² and 5 cm², respectively. The thickness of both electrodes was about 2 μm.

Fig. 2 Standard potential versus reversible hydrogen potential (RHE) for each electrochemical reaction.

Fig. 3 Cross-section of the experimental apparatus.

Pt/Ba/Al₂O₃ catalyst^{22, 23)} was set on the Pt plated cathode for the reduction of NO under O₂-rich conditions. Pt/Ba/Al₂O₃ was prepared by the following process: γ-Al₂O₃ powder was added into platinum dinitro diamine solution and stirred for 3 hrs. After evaporating the water, the resulting powder was calcined in air at 300°C for 3hrs. The powder was put into barium acetate solution and treated in the same way to obtain Pt/Ba/Al₂O₃ catalyst. The composition of this catalyst was 1.2 wt% Pt, 25.1 wt% Ba and 73.7 wt% Al₂O₃. Because the specific surface area of γ-Al₂O₃ powder was about 170 m²/g, Pt and Ba were considered to be dispersed well on γ-Al₂O₃. By XRD measurement, it was revealed that Ba on the catalyst existed as BaCO₃. Pt/Ba/Al₂O₃ catalyst and Pt paste (U-3820, N.E. Chemcat corp.) were mixed well, and then spread on the Pt plated cathode, and finally calcined at 800°C. After the calcination, the weight fractions of Pt/Ba/Al₂O₃ catalyst and Pt of Pt paste were 17 wt% and 83 wt%, respectively. The amount of Pt/Ba/Al₂O₃ catalyst was 60 mg.

The anode chamber and cathode chamber were constructed as shown in Fig.3. The gas mixture with 90% H₂O and 10% air was introduced into the anode chamber at a rate of 200 ml/min. The reference electrode in this gas showed the equilibrium potential among H₂O, O₂ and proton, according to equation (7).

Inert gases with or without NO and O₂ were introduced to the cathode at a rate of 30 ml/min. Direct current was applied galvanostatically to the cell. Experiments were carried out in the temperature range from 400 to 600°C at the atmospheric pressure. Gas chromatography with porapak Q and molecular sieve 5A columns was used to analyze the concentrations of H₂, N₂, O₂ and N₂O. The concentrations of NO_x and NH₃ were measured by Saltzman method and an absorbing-type gas detector (GASTEC Co. No.3L, 3M), respectively.

3 Results and Discussion

The results of the cell without catalyst, for which the cathode was pure Pt plated electrode, are described first.

Pure Ar gas was introduced to the cathode as a carrier gas. The H₂-production rate was measured at 450°C, and the result is shown in Fig. 4. The broken line represents 100% efficiency determined by Faraday's law. The efficiency higher than 90% was obtained for the current densities between 0 and 4 mA cm⁻². The same results were obtained at all temperatures under investigation. These results indicate that the present system can efficiently produce hydrogen which could be used as a reducing agent for NO.

Figure 5 shows the dependence of the NO-removal efficiency on current density when He gas containing 1000 ppm NO was introduced to the cathode at 450°C. The NO-removal efficiency is defined as the ratio of the amount of removed NO to that of supplied NO according to equation (8).

$$\text{NO-removal efficiency} = \text{removed NO} / \text{supplied NO} \quad (8)$$

Fig. 4 Change in H_2 production rate with current density. Temp.: 450°C . The broken line represents 100% efficiency determined by Faraday's law.

Fig. 5 Change in NO removal efficiency* and concentrations of the products with current density. Feed gas: 1000 ppm NO in He. Temp.: 450°C . *NO removal efficiency = Removed NO / Supplied NO.

The efficiency increased with increasing current density, and reached to 100% at current densities higher than 1.2 mA cm^{-2} . The main products were N_2O and N_2 at low current densities, and N_2 and NH_3 at high current densities. The total amount of nitrogen in the products was equal to that of the removed NO.

Figure 6 shows NO- and O_2 -removal efficiencies when He gas containing 1000 ppm O_2 and 1000 ppm NO was introduced to the cathode at 450°C . At lower current densities, the reduction of O_2 was predominant. NO reduction started at current densities higher than 1.6 mA cm^{-2} at which most of O_2 was removed. The reaction products of the NO reduction were similar to those of Fig. 5. The total amount of nitrogen in the products was also equal to that of the removed NO. The preferable reduction of O_2 to NO was observed throughout the experimental temperature range.

The current dependence of cathode potentials against the reference electrode is shown in Fig. 7. The cathode potentials of the cell for reducing NO and O_2 were higher than those of the cell for producing H_2 . This suggests that NO and O_2 were not chemically reduced by H_2 gas. Therefore, NO and O_2 are considered to be electrochemically reduced by protons according to equations (2)~(5), or chemically reduced by atomic hydrogen adsorbed on Pt. As shown in Fig. 2, NO was expected to be

Fig. 6 Change in O_2 and NO removal efficiency* and concentrations of the products with current density. Feed gas: 1000 ppm O_2 and 1000 ppm NO in He. Temp.: 450°C . * O_2 (NO) removal efficiency = Removed O_2 (NO) / Supplied O_2 (NO).

Fig. 7 Current dependence of cathode potential at 450°C . $\circ$: H_2 production (Feed gas: pure Ar), $\triangle$: NO reduction (Feed gas: 1000 ppm NO in He), $\diamond$: O_2 and NO reduction (Feed gas: 1000 ppm O_2 and 1000 ppm NO in He).

reduced easier than O_2 . However, the experimental results showed that O_2 was reduced easier than NO. It seems that the activation energy for NO reduction is very high.

Figure 8 shows the temperature dependence of the NO-removal efficiency when He gas containing 8% O_2 and 1000 ppm NO ($\text{O}_2/\text{NO}=80$) was introduced to the cathode. The concentrations of O_2 and NO correspond to those of exhaust gases from combustion engines operating under the lean-burn condition with the air-fuel ratio of about 20. The current density was 2.4 mA cm^{-2} . If H_2 gas is produced in this atmosphere containing O_2 and NO, the amount of H_2 gas produced at this current density will be three times of the amount of NO and only one-twenty seventh of the amount of O_2 in the cathode gas.

NO was not removed at the pure Pt plated cathode, as shown in Fig. 8 (open-circle). In the cell with the Pt/Ba/ Al_2O_3 catalyst on the Pt plated cathode, however, NO could be removed. The NO-removal efficiency reached up to 20% at 400°C . N_2 and N_2O were detected in the outlet gas as products of the NO reduction and NH_3 was not detected. The NO-removal rate and the N_2 - and N_2O -formation rates were plotted in Fig. 9. The NO-removal

Fig. 8 Temperature dependence of NO removal efficiency* for the cell with pure Pt cathode and the cell with Pt/Ba/Al₂O₃ catalyst on Pt cathode. Feed gas: 1000 ppm NO and 8% O₂ in He. Current density: 2.4 mA cm⁻². *NO removal efficiency = Removed NO/Supplied NO.

Fig. 9 Temperature dependence of NO removal rate, N₂ and N₂O formation rate for the cell with Pt/Ba/Al₂O₃ catalyst. Feed gas: 1000 ppm NO and 8% O₂ in He. Current density: 2.4 mA cm⁻².

efficiency and N₂-formation rate of this cell with the Pt/Ba/Al₂O₃ catalyst were higher than those of the cell with "Pt sponge + Sr/Al₂O₃" catalyst previously reported.¹⁹⁾ About 82% of the removed NO was reduced to N₂ and N₂O at 400°C as shown in Fig.9. The rest (18%) of the removed NO is considered to be absorbed into the catalyst because alkaline-earth elements such as Ba and Sr are known to absorb NO and to form nitrate, such as Ba(NO₃)₂ and Sr(NO₃)₂, when O₂ coexists.²²⁻²⁴⁾

The dependence of NO-removal rate and N₂- and N₂O-formation rate on current density at 400°C is shown in Fig.10. When the cell with the Pt/Ba/Al₂O₃ catalyst was used, the NO-removal rate and the N₂- and N₂O-formation rate increased with increasing current density. On the other hand, when the cell with the pure Pt cathode (○) was used, NO was not removed even at 4 mA cm⁻². All hydrogen produced was thought to react with O₂ and not with NO.

Figure 11 shows the cathode potential of the cells used in these experiments. This figure also shows the cathode potential of the cell for producing H₂ gas in case pure Ar gas was introduced to the cathode. These results suggest that H₂ gas might not be produced when the cell with the Pt/Ba/Al₂O₃ removed NO, and that NO might

Fig. 10 Change in NO removal rate, N₂ and N₂O formation rate with current density. Feed gas: 1000 ppm NO and 8% O₂ in He. Temp.: 400°C. △ : NO removal rate of Pt/Ba/Al₂O₃ | Pt | Sr(Zr,Yb)O₃ | Pt cell, ▲ and ◆ : N₂ and N₂O formation rate of Pt/Ba/Al₂O₃ | Pt | Sr(Zr,Yb)O₃ | Pt cell, ○ : NO removal rate of Pt | Sr(Zr,Yb)O₃ | Pt cell.

Fig. 11 Current dependence of cathode potential at 400°C. ○ : pure Pt cathode (Feed gas: pure Ar, H₂ production), ● : pure Pt cathode (Feed gas: 8% O₂ and 1000 ppm NO in He), □ : Pt/Ba/Al₂O₃ catalyst on Pt plated cathode (Feed gas: 8% O₂ and 1000 ppm NO in He).

be reduced electrochemically by proton or chemically by atomic hydrogen adsorbed on Pt. Furthermore, when He gas containing NO and O₂ was introduced into the cathode, the cathode potential of the cell with the Pt/Ba/Al₂O₃ catalyst was lower than that of the cell with the pure Pt cathode. This indicates that the Pt/Ba/Al₂O₃ catalyst inhibited the reaction between O₂ and proton.

As mentioned above, O₂ should be necessary for the absorption of NO into Ba and for the formation of Ba(NO₃)₂ according to equation (9).

It is considered that the reduction of O₂ by proton was inhibited because O₂ was used for the absorption of NO into Ba.

If the absorption of NO into Ba is not involved in the NO reduction, NO will be reduced until all Ba absorbs NO to form Ba(NO₃)₂ and O₂ reduction is started. Considering the flow rate of NO gas fed into the cathode and the amount of the Pt/Ba/Al₂O₃ catalyst, it will take three

hours for the conversion of all Ba into $\text{Ba}(\text{NO}_3)_2$. However, when this NO reduction experiment was repeated with the same cell for more than three hours, the same results (NO-removal efficiency, N_2 - and N_2O -formation rate) were obtained. Therefore, the possible reaction cycle is: (i) NO is absorbed into Ba, (ii) absorbed NO is reduced to N_2 or N_2O by proton or atomic hydrogen, (iii) Ba is again formed, acting as the NO absorption site. In this case, the related electrochemical reaction will be written as equation (6). However, Ba in the Pt/Ba/ Al_2O_3 catalyst did not directly contact with the protonic conducting electrolyte because this catalyst was laid on the Pt plated electrode. Therefore, the possible NO reduction mechanism is the chemical reaction with atomic hydrogen rather than the electrochemical reaction with proton. Figure 12 shows a schematic diagram of NO reduction mechanism using the steam electrolysis cell with the Pt/Ba/ Al_2O_3 catalyst under O_2 -rich atmospheres.

From these results, this new method for NO reduction using a steam electrolysis cell has been verified. Because this method can produce hydrogen as a reducing agent of NO by steam electrolysis, it will be expected that this cell can be applied to reduce NO in the exhaust gases of lean-burn engines containing a small amount of the reductive components such as CO and hydrocarbons. Further studies in this field are needed to improve the performance of this cell as a NO-removal device.

4 Conclusion

A steam electrolysis cell was constructed using a perovskite-type protonic conductor, $\text{SrZr}_{0.9}\text{Yb}_{0.1}\text{O}_{3-\alpha}$, as an electrolyte. The present system efficiently produced H_2 by steam electrolysis in the temperature range from 400 to 600°C. When gases containing NO were supplied to the cathode, NO was removed effectively. The reduction products were N_2O , N_2 and NH_3 depending on current density. Because the cathode potentials of the cell for reducing NO were higher than those of the cell for producing H_2 , NO is considered to be reduced by proton or atomic hydrogen. Combining the Pt/Ba/ Al_2O_3 catalyst with this electrolysis cell made it possible to reduce NO even in oxidizing atmospheres. The reduction of O_2 might be inhibited due to the absorption of NO and O_2 into Ba, and the absorbed NO into Ba might be reduced

Fig. 12 Schematic diagram of NO reduction using a steam electrolysis cell with Pt/Ba/ Al_2O_3 catalyst.

to N_2 by atomic hydrogen.

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