Influence of NO_x adsorbent on NO_x decomposition property of Gd doped CeO₂ based electrochemical cells

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We attempted to fabricate and evaluate a new nitrogen oxides (NO_x) decomposition electrochemical cell with the additional NO_x adsorbent and investigated a cell operating method to achieve a low temperature operation in the presence of excess O₂. To clarify the arrangement that improves the effect of NO_x adsorbent on NO_x decomposition property at low temperature range, we carried out the NO_x decomposition measurements on three kinds of electrochemical cells. As a result, NO_x adsorbent have drastically improved the NO gas decomposition properties though the current values of each cell were almost the same. The NO gas decomposition by a GDC (10 mol % Gd doped CeO₂) based cell with the NO_x adsorbent took onset around 225°C. Highly effective NO gas decomposition at a low temperature range (<300°C) has been possible by using the electrochemical cell which saturated aqueous solution of KNO₃ penetrated into the catalytic layer electrodes after the cell operation. It was clarified that the frequency characteristic was different depending on the cell-operating mode of applied AC voltage.

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1. Introduction

Nitrogen oxides (NO_x), NO and NO₂ are implicated as a cause of the formation of acid rain and a tropospheric ozone (the principal toxic component of smog and a greenhouse gas).^{1),2)} The major known source of NO_x is fuel combustion and biomass burning. Air pollution by NO_x in combustion waste causes serious environmental problems in urban areas. Therefore, development of innovative NO_x decomposition technology is strongly required in the world. The reduction of NO_x emissions has become one of the greatest challenges in environment protection.^{3),4)} This is why the different methods of NO_x decomposition are intensely studied by numerous groups from academic as well as industrial research laboratories.^{5),6)} The main activities of scientific groups working in the field of NO_x decomposition are concentrated on the catalyst technology such as urea-based selective catalytic reduction (SCR) system. However, There are some issues on the catalytic NO_x decomposition. However, secondary pollutant remains a matter of grave concern for the catalytic NO_x decomposition. Additional reducing reagents for the catalytic reaction such as hydrocarbons, CO, H₂ or ammonia can lead to the production of secondary pollutants like oxygenated hydrocarbons, CO, CO₂, N₂O or ammonia or, even, as was often reported in the past, cyanate and isocyanate compounds.

On the other hand, electrochemical reaction is one promising technology of active reduction and oxidation on the electrode using electric power. Without coexisting oxygen the successful decomposition of NO gas into oxygen and nitrogen in a primitive electrochemical cell was first demonstrated over 25 years ago.^{7),8)} They showed NO_x decomposition using O₂ pumping through the ion conducting materials such as Y-doped ZrO₂ (YSZ) at high

voltage. However, electrochemical reductions with the primitive electrochemical cells show a low selectivity for NO reduction in the presence of the excess oxygen and it should be operated in high temperature range (<600°C) to attain the NO_x reduction rate required for practical use. Thus, it can't be used for practical application.

To solve the problem of effective electrochemical reduction of nitric oxide in the presence of the excess oxygen S. Bredikhin et al.⁹⁾⁻¹¹⁾ proposed the concept of artificially designed multilayer structure, which should operate as a cathode with high selectivity. We recently proposed to use an electrochemical cell with additional NO_x adsorption layer deposited on the top of the multilayer cathode. The cell can be represented by following cell arrangement:

To clarify the capability of a NO_x adsorption layer on the multilayer cathode, we carried out the NO_x decomposition measurements of the YSZ based electrochemical cells with and without a NO_x adsorbent at a fixed operating voltage. As a result, NO_x adsorption layers have improved the NO_x decomposition properties though the current values of each cell were almost the same.¹²⁾

In this study, an attempt was made to correlate the NO_x decomposition property with an appropriate and effective design of a NO_x adsorption site and a cell operating method for a further improvement of electrochemical NO_x decomposition.

2. Experimental

Electrochemical cell with multi-layer catalytic electrodes was prepared by using a conventional screen printing method. GDC (10 mol % Gd doped CeO₂) disk (20 mm in diameter and 0.5 mm thick) was used as a solid electrolyte. A mixed paste of Pt-GDC with 40 mol % of Pt was screen-printed on the both surfaces of

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GDC electrolyte disk as the collector electrode and calcined at 1150°C for an hour. Then the mixed oxides paste of NiO–GDC with 55 mol % of NiO was screen-printed over the collector electrodes and sintered at 1450°C for 5 h. The GDC paste was screen-printed over the catalytic layer as the cover layer and sintered at 1450°C for 3 h. Self-assembled nano-pores and nano-Ni particles are obtained from the reduction of NiO in the vicinity of GDC–NiO interfacial regions in the catalytic layer by the cell operation. This reduced structure provides a way to suppress the unwanted reaction of oxygen gas decomposition and to increase many times the desirable reaction of NO_x decomposition.^{10),11)} Cover layer increases the rate of reduction of NiO to Ni in the catalytic layer.¹¹⁾ Finally, NO_x adsorbent was coated or penetrated to the cell by the dip coating method and calcined at 600°C for 1 h. We chose two systems for NO_x adsorbent. One is the Pt/K/Al₂O₃ adsorbent was prepared from a Al₂O₃ (Merck, p.a., specific surface area = 10 m² g⁻¹) support suspension in water, to which a solution containing KNO₃ and with aqueous solutions of platinum nitrate [Pt(NO₃)₂] was added, in order to obtain a load of 10 wt % of K and 3 wt % of Pt. The mixture was heated while being vigorously stirred until a paste was achieved, which was dried in an oven for 24 h at 200°C and crushed and calcined at 600°C for 2 h. This is almost the same composition as the general NO_x adsorber catalyst used for the gasoline engine. Another is the saturated aqueous solution of KNO₃. It is known that the alkaline metal and the alkaline-earth metal function as an effective adsorption site of NO_x.

The electrochemical cell was set in the quartz tube reactor and connected to the potentiostat (SI1287, SOLARTRON) or the

function generator with the high speed bipolar amplifier and a digital multimeter, to investigate the applied current dependence of NO decomposition behavior. The cell operation was performed in the temperature range of 200–500°C by passing a mixed gas with 1000 ppm of NO and 10% of O₂ in He through the cell at a gas flow rate of 50 ml/min. Mass flow controllers were employed to obtain a well-defined gas mixture of NO, O₂ and He. The concentrations of NO and N₂ in the outlet gas ([NO]_{out}) were monitored using an on-line NO_x (NO, NO₂ and N₂O) gas analyser (Best Instruments BCL-100uH, BCU-100uH) and a gas chromatograph (CHROMPACK Micro-GC CP 2002), respectively. The nitrogen monoxide decomposition rate (ΔNO) based on these measurements was calculated as:

$$\Delta\text{NO} = ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}})/[\text{NO}]_{\text{in}} \quad (2)$$

3. Results and discussion conclusions

To clarify the arrangement that improves the effect of NO_x adsorbent on NO_x decomposition property at low temperature range, we carried out the NO_x decomposition measurements on three kinds of electrochemical cells. The first is an electrochemical cell that has a fundamental configuration with multilayer electro-catalytic electrodes. Second is an electrochemical cell with the Pt/K/Al₂O₃ adsorbent layers deposited on the top of the multilayer electro-catalytic electrodes. Third is an electrochemical cell that the saturated aqueous solution of KNO₃ penetrated into the self-assembled nano-pores in the catalytic layers after cell operation. These cells can be represented as follows:

NiO–GDC (catalytic layer) | Pt–GDC (collector electrode) | GDC (electrolyte) |

Pt–GDC (collector electrode) | NiO–GDC (catalytic layer) (3)

Pt/K/Al₂O (NO_x adsorbent) | NiO–GDC | Pt–GDC | GDC | Pt–GDC | NiO–GDC | Pt/K/Al₂O (NO_x adsorbent) (4)

NiO–GDC with KNO₃ | Pt–GDC | GDC | Pt–GDC | NiO–GDC with KNO₃ (5)

The cell operation was performed in the temperature range of 200–500°C by passing a mixed gas with 1000 ppm of NO and 10% of O₂ in He through the cell at a gas flow rate of 50 ml/min.

Figure 1 shows the dependency of NO gas decomposition properties to the cell operating temperature under applied a

Fig. 1. NO decomposition properties dependence of operating temperature.

square-wave voltage ($U = \pm 4$ V) with modulating frequency of 0.25 Hz. GDC is one oxygen ion conductive material, indicating high conductivity at low temperature. For the purpose of decreasing operation temperature, GDC is suitable for the electrolyte. And the catalytic layer with self-assembled nano-pores and nano-Ni particles provides a way to increase the desirable reaction (NO gas decomposition) many times in the presence of excess O₂. However, The electrochemical cell without any NO_x adsorbent was shown very low effective NO gas decomposition properties in the presence of excess oxygen. This is because the current efficiency for the NO gas decomposition decreases with an increase in the oxygen ion conductivity of electrolyte. Increase in oxygen ion conductivity of the electrochemical cell not only decreases operating temperature, but also increases undesirable reaction of coexistent O₂ gas decomposition at the F-type centers.¹³⁾ In contrast, the NO_x adsorbents have drastically improved the NO gas decomposition properties though the current values of each cell were almost the same. The NO decomposition by the electrochemical cell with the NO_x adsorbent took onset around 225°C. Highly effective NO gas decomposition at a low temperature range (<300°C) has been possible by using the electrochemical cell which saturated aqueous solution of KNO₃ penetrated into the multilayer electro-catalytic electrodes after the cell operation. As for the electrochemical cell with the Pt/K/Al₂O₃ adsorbent layer, the adsorbent is arranged at a position far from a reaction site in the multilayer

Fig. 2. Dependency of NO_x decomposition to the modulation frequency of applied square-wave voltage at 300°C .

electro-catalytic electrodes. NO_x decomposition efficiency decreased with increase of the distance between NO_x adsorbent and reaction site. These results suggest that the arrangement of adsorption sites (NO_x adsorbent) to be adjacent to a reaction site is effective for improvement of NO_x decomposition efficiency. It is expected that the NO_x adsorbent provide a high concentration of NO_x to the reaction site (F-type centers and surface of nano-Ni particles). Especially, it is thought that the reaction at F-type center with low selectivity of NO_x decomposition dramatically improved. And, the NO_x decomposition efficiency changes in proportion to the adsorbability of NO_x adsorbent.

To obtain an additional indication about the NO_x adsorbent, we measured the operating voltage condition dependence of NO gas decomposition property at a low temperature range. **Figure 2** shows the dependency of NO gas decomposition to the modulation frequency of operating voltage for an electrochemical cell with the KNO_3 adsorbent. On an applied square-wave voltage, it is obvious that the NO decomposition rate became the maximum value when a square-wave voltage of $\pm 4\text{ V}$ with the modulation frequency range of $0.5\text{--}0.1\text{ Hz}$ were applied at 300°C . In the modulation frequency range of $0.5\text{--}0.1\text{ Hz}$, adsorption and decomposition rate of NO in the catalytic layer is balanced. However, NO_x gases are not adsorbed to the NO_x adsorbent enough when the NO_x decomposes continuously in the low frequency range under 0.04 Hz . Therefore, the current efficiency decreases with a decrease in the concentration of NO_x in the catalytic layer. And, the NO decomposition rate decreases with an increase in the modulation frequency over 0.5 Hz . The electrical current that flowed into the cell was almost constant without depending on the modulating frequency. Therefore, it seems that the amount of NO decomposition decreased because the reaction rate of NO_x decomposition at the electrode is slow. On an applied sinusoidal voltage, an increase in the nitrogen oxide decomposition rate according to a decrease in the modulation frequency was observed. Because the amount of electric charge is smaller than the square wave operation, the NO decomposition property was low in the sinusoidal voltage operation. A decrease in the NO decomposition reaction was not observed in the area of a low modulating frequency.

Frequency characteristic was different depending on the operating mode of applied voltage and the operating temperature.

Fig. 3. Time dependence of the NO gas decomposition properties of an electrochemical cell with the KNO_3 on an applied sinusoidal voltage of $\pm 4\text{ V}$ at 300°C .

Fig. 4. Time dependence of the NO decomposition properties of an electrochemical cell with the KNO_3 on a square-wave voltage of $\pm 4\text{ V}$ at 300°C .

It is expected that the adsorption and desorption rate of NO_x molecule on an adsorbent strongly affects to the NO_x decomposition property. Therefore, it is necessary to optimize the operation condition of the applied voltage and the operating temperature to each NO_x adsorbent. **Figures 3 and 4** shows the time dependence of the NO gas decomposition properties of an electrochemical cell with the KNO_3 on an applied sinusoidal voltage and square-wave voltage of $\pm 4\text{ V}$, respectively. The NO decomposition rates became unstable in the low modulation frequency range under 0.04 Hz though the NO decomposition rates were stable at the high modulation frequency range. In the condition of the same modulation frequency, the NO_x decomposition rates of the sinusoidal voltage operation oscillated with a larger amplitude in comparison with the square-wave voltage operation. On an applied sinusoidal voltage, there is a condition of less than operation voltage necessary for the NO decomposition reaction, the periodic amplitude of the NO_x decomposition rates on the sinusoidal voltage has changed by the twice the modulating frequency of applied voltage.

Fig. 5. Time dependence of the NO decomposition properties of an electrochemical cell with the KNO₃ on an applied sinusoidal voltage of ± 4 V at 300°C.

Two electrochemical cells with the KNO₃ that had been made at the same preparation procedure were measured under the same operating condition. The penetration condition of the saturated aqueous solution of KNO₃ into the catalytic layer was slightly different for individual difference of each electrochemical cell. As a result, the profile of the NO gas decomposition rates was large different though the mean value of the NO gas decomposition rates was almost the same (Fig. 5). This result suggests that the slight difference of arrangement on the NO_x adsorbent in the electrode layers strongly affects to the NO gas decomposition property. Therefore, it is necessary to understand and control the microstructure of NO_x adsorbent in the catalytic layer to prevent adsorption and decomposition of O₂ on the reaction sites for the improvement of the NO decomposition efficiency.

4. Conclusions

We attempted to fabricate and evaluate a new type of NO_x decomposition Gd doped CeO₂ based electrochemical cell with the additional NO_x adsorbent and investigated a cell operating method to achieve a low temperature operation in the presence of excess oxygen. It was clarified that the arrangement of adsorption sites (NO_x adsorbent) to be adjacent to a reaction sites is

necessary for improvement of NO_x decomposition efficiency. And the NO_x adsorbent provide a high concentration of NO_x to the reaction sites in the catalytic layer even if the cell is in the presence of excess oxygen. Highly effective NO_x decomposition at 300°C has been possible by optimizing a NO_x adsorbent and an operation voltage condition. The slight difference of arrangement of the NO_x adsorbent in the electrode strongly influences the NO_x decomposition property. These results indicate that the new type of electrochemical cell for NO_x decomposition would represent the most attractive solution in emission control of diesel, because the reaction does not require that any reactant be added to NO_x exhaust gas and could potentially lead to the formation of only N₂ and O₂ at low temperature. From our point of view, these systems should substitute traditional catalytic systems for exhaust gas purification.

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