CHEMISTRY LETTERS, pp. 927-930, 1994.

Electrochemical Removal of NO and CH_4 from Oxidizing Atmosphere

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An electrochemical cell, Pd | YSZ | Pd, was constructed to remove both NO and CH_4 from an oxidizing atmosphere. When the direct current was supplied to the cell at 700 ℃ in the reactant flow containing 1000 ppm NO, 1000 ppm CH_4 and an excess amount of O_2, NO was reduced to N_2 at the cathode, and CH_4 was oxidized to COx at the anode.

Removal of both NO and hydrocarbons from exhaust gases, which contain a significant amount of O_2, is an important subject in environmental chemistry. Catalytic reduction of NO by hydrocarbons has been studied using various types of catalysts.[1-4] However, no report has been published on electrolysis of a trace amount of NO in oxidizing atmospheres. Huggins and co-workers achieved electrochemical reduction of pure NO to N_2 using a zirconia-based solid electrolyte, in which two porous Pt metals were employed as electrode materials and voltages of above 1 V were applied to the cell at 600 to 800 ℃ in the absence of O_2. They describe that NO is decomposed on electrochemically reduced surface, F-center, of zirconia. If so, the F-center will not be formed on the zirconia surface in the presence of excess O_2. Since the exhaust gases generally contain H_2O, CO_2, hydrocarbons, etc. besides NO and O_2, there arise additional problems to be solved from the practical standpoints: (1) in the electrolysis process of NO in such a cell, H_2O and CO_2 will be competitively electrolyzed. Therefore, the electrolysis of the latter two substances must be minimized. (2) hydrocarbons as well as NO are required to be removed from the exhaust gases. The author will report that an electrochemical cell, Pd | YSZ | Pd, satisfies above demands.

YSZ sintered compact was prepared by pressing 8 mol% yttria-doped zirconia powder (Tosoh TZ-8Y) at 2×10^3 Kg cm^{-2} and then calcining it at 1550 ℃ for 10 h. The sintered compact was cut into a disc with 12 mm in diameter and 0.5 mm in thickness. Two porous Pd electrodes with 0.5 cm^2 in area were baked at 700 ℃ on both sides of the YSZ disc. Two Pt wires which served as output terminals for two electrodes were connected to a galvanostat. The electrochemical reaction was usually carried out using a cell as shown in Fig. 1 (a) by passing a gas mixture of 1000 ppm NO, 1000 ppm CH_4, 2% O_2, 5% H_2O and 5% CO_2 in argon at a rate of 50 ml min^{-1}. The reaction temperature was 700 ℃. The outlet gases were analyzed by gas chromatography and mass spectroscopy. Another cell as shown in Fig. 1 (b) was constructed in order to evaluate the degree of reduction of NO at the cathode and oxidation of CH_4 at the anode independently. The YSZ disc of this cell served as a diaphragm between two electrode compartments. Each compartment was sealed by a glass ring gasket. The reactant gas of 1000 ppm NO, 2% O_2, 5% H_2O and 5% CO_2 was introduced into the cathode compartment, and the reactant gas of 1000 ppm CH_4, 2% O_2, 5% H_2O and 5% CO_2 was introduced into the anode compartments. The other reaction conditions were the same as those of the cell (a) in Fig. 1.

Figure 2 shows the amounts of NO and CH_4 in the outlet gas of the cell (a) obtained under open- and closed-circuit conditions at 700 ℃. At the open-circuit, all NO was collected at the outlet, while 76% of CH_4 was oxidatively decomposed. By supplying the direct current, the amount of NO was reduced to one-half of its initial value, and most of CH_4 was oxidized.

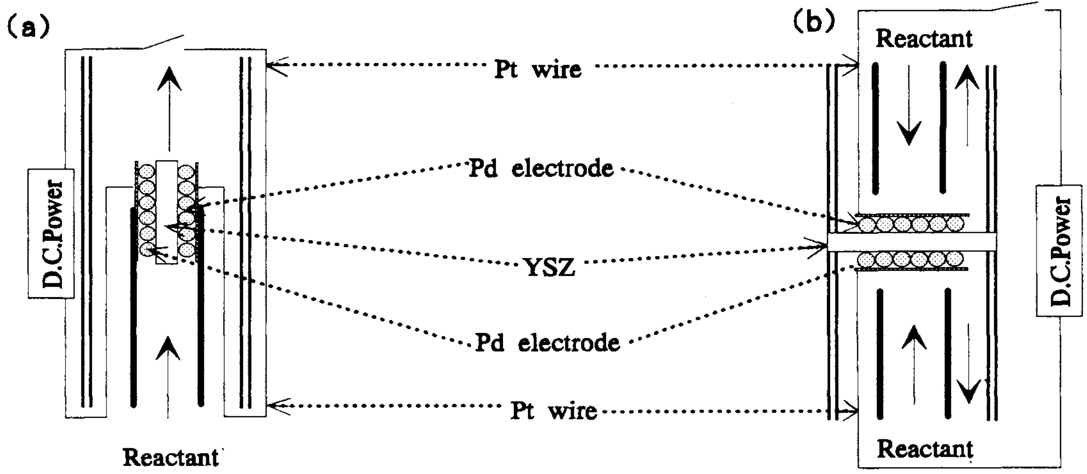

Fig. 1. Schematic illustrations of two types of cells (a) and (b).

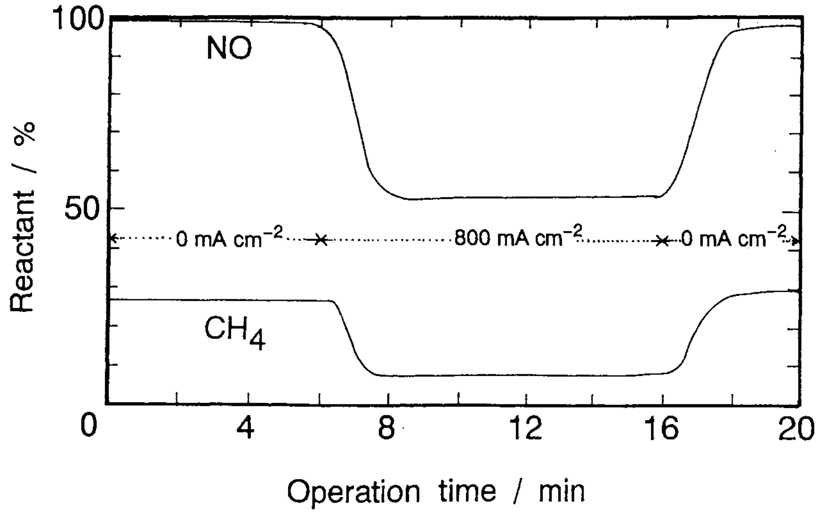

Fig. 2. Change in the amounts of NO and CH_4 caused by passing the direct current through the cell (a): the amounts of reactants are calibrated to their initial values.

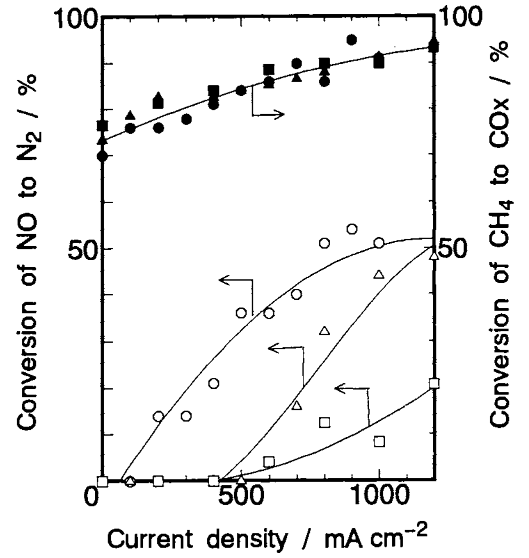

Fig. 3. Effect of concentration of O_2 on NO and CH_4 conversions: concentration of O_2 is 2% ○●, 6.6% △▲ and 10% □■; open and closed symbols are NO and CH_4 conversions, respectively.

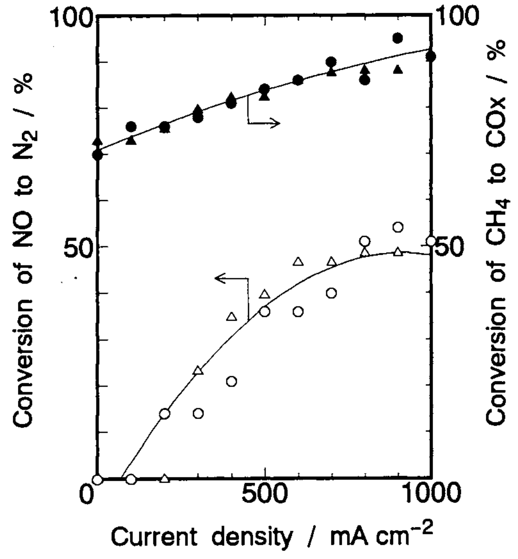

Fig. 4. Effect of presence of H_2O and CO_2 on NO and CH_4 conversions: 5% H_2O and 5% CO_2 ○●, and 0% H_2O and 0% CO_2 △▲; open and closed symbols are NO and CH_4 conversions, respectively.

Figure 3 shows the effect of the concentration of O_2 in the reactant gas on the conversions of NO and CH_4. In the concentration range of 2 to 10%, the oxidation of CH_4 to COx was independent of the concentration of O_2, while the degree of the reduction of NO to N_2 decreased with increasing the concentration of O_2. Figure 4 shows the effect of the presence of H_2O and CO_2 in the reactant gas on the conversions of NO and CH_4. Neither the reduction of NO to N_2 nor the oxidation of CH_4 to COx was affected by the presence of H_2O and CO_2.

The reduction of NO to N_2 at the cathode and the oxidation of CH_4 to COx at the anode were evaluated separately using the cell (b). Results are summarized in Fig. 5. As the current density increased, the concentration of NO and O_2 in the outlet gas of the cathode compartment decreased with the generations of N_2 and a small amount of H_2. Since the reduction of NO to N_2 was not affected by the presence of H_2O, as shown in Fig. 4, it is unlikely that NO is reduced by the generated H_2. NO would be electrolyzed at the cathode. Furthermore, NO was electrolyzed even at small current densities in the presence of a high concentration of O_2, suggesting that NO was not electrolyzed on the F-center of YSZ. Amirnazmi et al. proposed that the catalytic decomposition of NO was inhibited by the presence of oxygen species chemisorbed on Pt catalysts.[6] Assuming that this inhibition would be the case for the Pd electrode, a clean Pd surface free from adsorbed oxygen would be formed by electrochemical pumping of O_2 from the cathode to the anode, which results in an increased number of active sites on the surface.

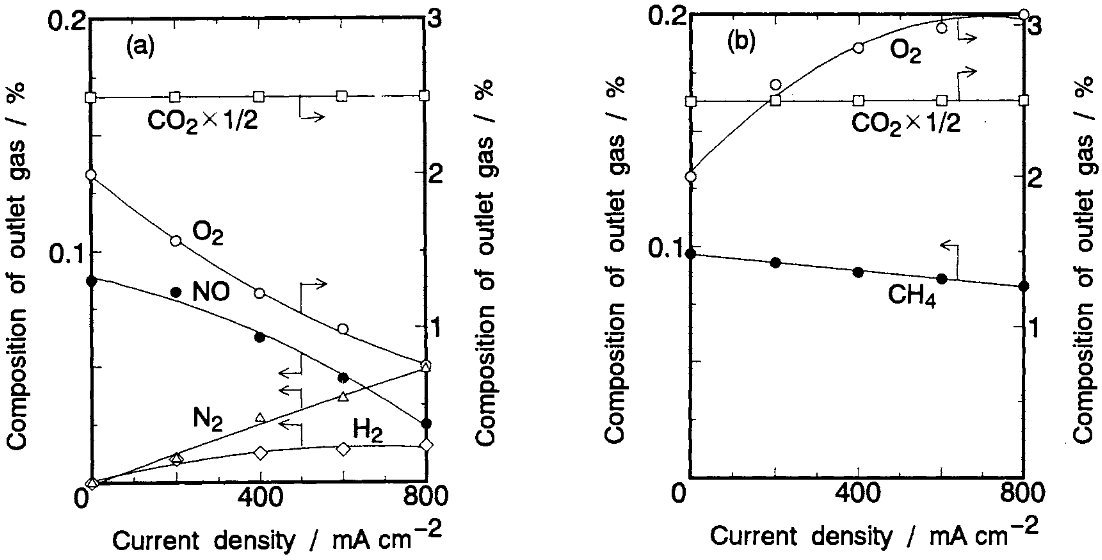

Fig. 5. Compositions of the outlet gas from cathode (a) and anode (b) in cell (b) in Fig. 1.

As the current density increased, the concentration of O_2 in the outlet gas of the anode compartment increased, whereas that of CH_4 decreased. This suggests that atomic oxygen is formed at the electrolyte/electrode/gas interface and directly reacts with CH_4. This hypothesis may be explained by the finding that the oxidation of CH_4 to COx is not dependent on the concentration of molecular oxygen, as shown in Fig. 3.

From the above results, it is found that NO is reduced to N_2 at the cathode of the cell (a) and simultaneously CH_4 is oxidized to COx at the anode. However, the NO conversion to N_2 cannot exceed 50%, since only half of the reactant gas passes through the cathode in such a single cell. It would be possible to enhance the ratio of the NO conversion to N_2 by constructing a cascade of several cells.

References

1) S. Sato, Y. Yu-u, H. Yahiro, N. Mizuno, and M. Iwamoto, *Appl. Catal.*, **70**, L1 (1991).
2) Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki, and T. Ito, *Catal. Lett.*, **6**, 239 (1990).
3) M. Misono and K. Kondo, *Chem. Lett.*, **1991**, 1001.
4) E. Kikuchi, K. Yogo, S. Tanaka, and M. Abe, *Chem. Lett.*, **1991**, 1063.
5) S. Pancharatnam, R. A. Huggins, and D. M. Mason, *J. Electrochem. Soc.*, **122**, 869 (1975).
6) A. Amirnazmi, J. E. Benson, and M. Boudart, *J. Catal.*, **30** 55 (1973).

(Received February 21, 1994)