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NO_x reduction with methane over mordenite supported palladium catalyst

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Abstract

Catalytic reduction of NO_x with small amounts of hydrocarbons in the presence of excess oxygen and water vapor have been studied over mordenite supported metal catalysts. Pd/mordenite catalyst was found to be very active for the reduction of NO_x with methane.

Keywords: NO_x reduction; Palladium

1. Introduction

Pollution caused by the emission of NO_x is one of the most important global environmental problems today.

Several methods of removing NO_x from exhaust gases, including selective catalytic reduction with ammonia (SCR) and catalytic reduction using three-way catalysts, have been adopted. These conventional methods cannot, however, be readily applied to lean-burn gas engines in cogeneration systems because ammonia is difficult to deal with due to its poisonous character and three-way catalysts are effective only in the absence of oxygen. Recently, although many researchers have been studying catalytic reduction of NO_x with hydrocarbons [1–5], favorable catalytic systems for gas engines have not yet been developed. In view of this, we have been studying and developing new catalysts for the reduction of NO_x with oxygenated compounds and hydrocarbons in an attempt to find a better way to remove NO_x from the exhaust gases of lean-burn gas engines in cogeneration systems [6].

This paper presents the results of studies of catalytic reduction of NO_x with methane over mordenite supported metal catalysts in the presence of excess oxygen and water vapor.

2. Experimental

Catalysts were prepared by an ion-exchange procedure. Catalytic activity measurements were carried out in a fixed-bed flow reactor under ambient pressure. Space velocity was 44 000 h^{-1}. The reaction mixture typically contained 91–180 ppm of NO, 910 ppm of CO, 6.4% of CO_2, 9.1% of O_2, 9.1% of H_2O, 2450 ppm of hydrocarbon (C_1 basis), diluted with N_2. The effluent gases were analyzed by a chemilumi-

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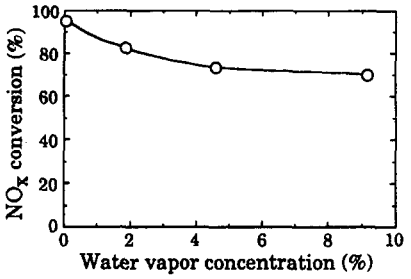

Fig. 1. Effect of water vapor. Catalyst: Pd/mordenite, Temperature: 673 K, [NO] = 200 ppm, [CO] = 1000 ppm, [CO_2] = 7%, [O_2] = 10%, [CH_4] = 2700 ppm (dry basis).

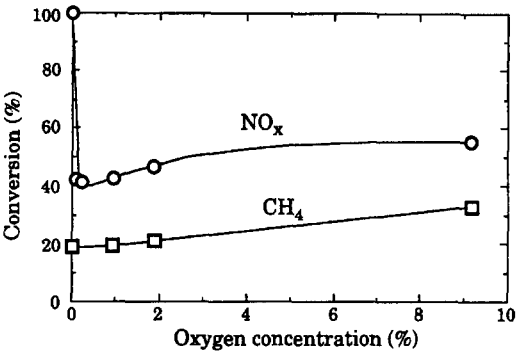

Fig. 2. Effect of oxygen. Catalyst: Pd/mordenite, Temperature: 673 K, [NO] = 91 ppm, [CO] = 910 ppm, [CO_2] = 6.4%, [H_2O] = 9.1%, [CH_4] = 2450 ppm.

nescence NO_x analyzer and a FID gas chromatograph. The NO_x conversion was calculated based on the differing NO_x concentrations at the inlet and outlet of the reactor.

3. Results and discussion

In the presence of excess oxygen, NO_x is reduced with hydrocarbons and oxygen over the catalyst, and the oxidation of hydrocarbons occurs simultaneously.

The effect of water vapor on NO_x reduction with methane over Pd/mordenite catalyst in the presence of excess oxygen is shown in Fig. 1. At 673 K, NO_x conversion in the absence of water vapor reaches 95%. NO_x conversion decreases with increasing the concentration of water vapor. The effect of water vapor is completely reversible. This suggests that the competitive adsorption of water and NO_x for active Pd sites depresses NO_x reduction with methane.

The effect of oxygen on NO_x reduction with methane over Pd/mordenite catalyst in the presence of water vapor is shown in Fig. 2. In the absence of oxygen, the Pd/mordenite catalyst is very active for NO_x reduction with methane, and in the presence of oxygen, NO_x conversion declines. However, although NO_x conversion is low at the low concentration of oxygen, when the concentration of oxygen is increased, NO_x conversion rises. The introduction of oxygen inhibits and then enhances NO_x reduction with methane over Pd/mordenite catalyst.

The results of NO_x reduction with methane over mordenite supported metal catalysts in the presence of excess oxygen and water vapor are shown in Fig. 3. NO is converted to N_2 and NO_2 with methane and oxygen over Co/mordenite catalyst, Cu/mordenite catalyst, Rh/mordenite catalyst and Pt/mordenite catalyst. However, over the Pd/mordenite catalyst, NO is almost completely converted to N_2. In the presence of excess oxygen and water vapor, the order of NO_x conversion is Pd/mordenite catalyst > Pt/mordenite catalyst > Rh/mordenite catalyst > Cu/mordenite catalyst >

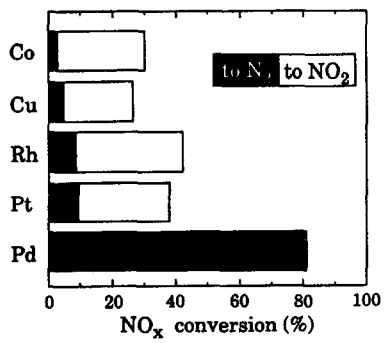

Fig. 3. Effect of supported metals on mordenite. Temperature: 673 K, [NO] = 180 ppm, [CO] = 910 ppm, [CO_2] = 6.4%, [O_2] = 9.1%, [H_2O] = 9.1%, [CH_4] = 2450 ppm.

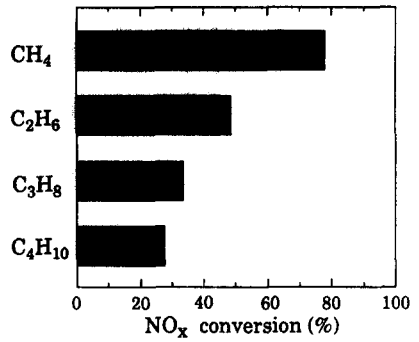

Fig. 4. Effect of reducing agents. Catalyst: Pd/mordenite, Temperature: 673 K, [NO] = 180 ppm, [CO] = 910 ppm, [CO_2] = 6.4%, [O_2] = 9.1%, [H_2O] = 9.1%, [Hydrocarbon] = 2450 ppm (C_1 basis).

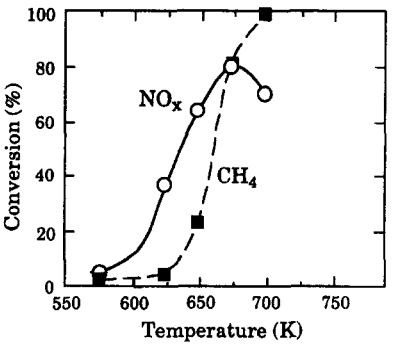

Fig. 5. Effect of reaction temperature. Catalyst: Pd/mordenite, [NO] = 180 ppm, [CO] = 910 ppm, [CO_2] = 6.4%, [O_2] = 9.1%, [H_2O] = 9.1%, [CH_4] = 2450 ppm.

Co/mordenite catalyst. The Pd/mordenite catalyst shows an extremely high activity and selectivity for NO_x reduction with methane. This suggests that methane is readily activated over Pd/mordenite catalyst in the presence of excess oxygen and water vapor.

Various hydrocarbons including methane, ethane, propane, and butane were investigated as NO_x reducing agents. Fig. 4 shows the results of NO_x reduction with various hydrocarbons over Pd/mordenite catalyst in the presence of excess oxygen and water vapor. Over Pd/mordenite catalyst, methane, which is the principal ingredient of fuel for gas engines, is the most effective reducing agent among saturated hydrocarbons in the presence of excess oxygen and water vapor. Ethane, propane and butane show lower effectiveness in NO_x reduction than methane because they are readily oxidized by oxygen.

Over Co/mordenite catalyst, propane acts effectively as a reducing agent comparable to that of methane in the presence of excess oxygen and water vapor, although it is lower.

Fig. 5 shows the results of NO_x reduction with methane over Pd/mordenite catalyst as a function of reaction temperature. NO_x conversion increases as the temperature rises to 673 K, with the maximum NO_x conversion reaching 80%. However, NO_x conversion falls when the temperature exceeds 673 K. The oxidation of methane by oxygen dominates the NO_x reduction at temperatures over 673 K. The methane conversion increases with reaction temperature. Because the methane oxidation rate becomes significant at high temperatures, the depressed NO_x conversion at temperature above 673 K is most likely the result of lowered methane concentrations in the catalyst bed.

NO_x reduction is dependent on methane concentration. As shown in Fig. 6, NO_x conversion increases with methane concentration. NO_x reduction rate is proportional to methane concentration. On the other hand, methane conversion decreases with increasing methane concentration.

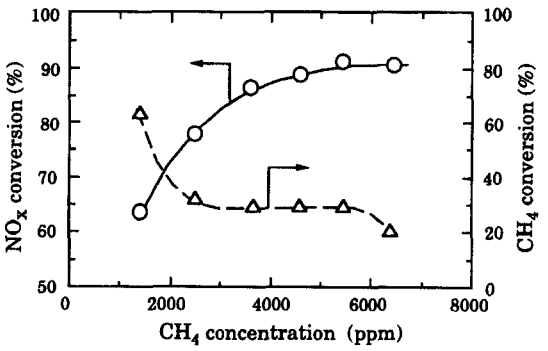

Fig. 6. Effect of methane concentration. Catalyst: Pd/mordenite, Temperature: 673 K, [NO] = 180 ppm, [CO] = 910 ppm, [CO_2] = 6.4%, [O_2] = 9.1%, [H_2O] = 9.1%, [CH_4] = 1350–6360 ppm.

4. Conclusion

We report that the Pd/mordenite catalyst is very active for the reduction of NO_x with methane in the presence of excess oxygen and vapor water. This conclusion provides an alternative approach for the emission control of lean-burn gas engines in cogeneration systems.

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