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Essential Role of Acidity in the Catalytic Reduction of Nitrogen Monoxide by Methane in the Presence of Oxygen over Palladium-Loaded Zeolites

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It has been demonstrated that the protonic acidity is essential for the reduction of nitrogen monoxide by methane over Pd ion-exchanged H-ZSM-5 (Pd/HZ), by the comparison of the reaction with that over Pd ion-exchanged Na-ZSM-5 (Pd/NaZ), having similar dispersion of palladium. It was further shown that the difference between the active Pd/HZ and the inactive Pd/NaZ is present in the reaction between NO_2 and CH_4.

We have previously reported that Pd ion-exchanged H-ZSM-5 (denoted by Pd/HZ) was active for NO-CH_4-O_2 reaction, while Pd ion-exchanged Na-ZSM-5 (Pd/NaZ) was inactive. On the other hand, both catalysts showed similar high activity for CH_4-O_2 reaction. These facts suggested that the presence of protonic acidity was essential for the NO-CH_4-O_2 reaction.[1] However, palladium in Pd/HZ was highly dispersed, as evidenced by the absence of XRD peaks assignable to Pd orPdO, while the dispersion was low for Pd/NaZ, as PdO was detected for Pd/NaZ. Hence, the possibility that the difference of activity was due to the difference in the Pd dispersion can not be excluded. In this study, we have attempted to differentiate the two possibilities by using Pd/HZ and Pd/NaZ having similar dispersion of Pd (or PdO) and further attempted to elucidate in which step of the reaction the acidity functions, since this is essential information for the development of an efficient catalyst for the reaction. Kikuchi et al. have also indicated that the acidity plays an important role in this reaction.[2]

H-ZSM-5 was prepared at room temperature by ion-exchange of Na-ZSM-5 (SiO_2/Al_2O_3 =23.3) in an aqueous solution of ammonium nitrate. After the exchange the solid was washed, dried at 110 °C for 12 h, and then calcined at 500 °C for 4 h in air. Pd/HZ(A) and Pd/NaZ(A) were prepared at room temperature by the ion-exchange of H-ZSM-5 and Na-ZSM-5 respectively, by using aqueous solution of $[Pd(NH_3)_4]Cl_2$. They were dried at 110 °C for 12 h and calcined in air at 500 °C for 2 h. The amounts of palladium loaded were about 1 wt%. Two more samples were prepared according to the scheme shown in Fig. 1. Pd/HZ(B) was prepared by the ion-exchange of Pd/NaZ(A) in an aqueous solution of ammonium nitrate, followed by drying and calcination at 500 °C for 2 h. Pd/NaZ(B) was prepared by the ion-exchange of Pd/HZ(A) using an aqueous solution of sodium nitrate.

The catalytic reactions were carried out with a flow reactor as described previously by passing a gas mixture of 1000 ppm NO or NO_2, 2000 ppm CH_4 and 2% O_2 in helium at a flow rate of 150 ml min^{-1} over 0.05 or 0.5 g catalysts. The effluent gases were analyzed by a gas chromato-graph (MS-5A and active carbon columns) and a NOx meter. The catalytic activities were evaluated by the conversion of NO (or NO_2) to N_2. X-ray diffraction of the samples was performed using CuKα radiation without any special pretreatment.

Figure 2 shows the results of XRD. The peak of PdO is located at 2θ = 33.9 deg. The other peaks are all due to ZSM-5. PdO was detected for Pd/NaZ(A) after calcination at 500 °C in air, while neither PdO nor Pd was detectable for Pd/HZ(A). The particle size of PdO in Pd/NaZ(A) was estimated to be about 20 nm from the line width. These peaks did not change after use for reaction. As for Pd/NaZ(B), PdO was observed after calcination at 500 °C, although neither PdO nor Pd was detected after drying at 110 °C. In the case of Pd/HZ(B) which was obtained from Pd/NaZ(A), the peak of PdO similar to the starting catalyst was also observed after calcination at 500 °C and the intensity did not change. Thus, Pd/NaZ(A), Pd/NaZ(B) and Pd/HZ(B) showed the similar Pd dispersion after calcination at 500 °C, although Pd/NaZ having high Pd dispersion was not obtained. Therefore, the effect of acidity may be determined unambiguously by comparing Pd/HZ(B) and Pd/NaZ(A), of which the PdO dispersion was

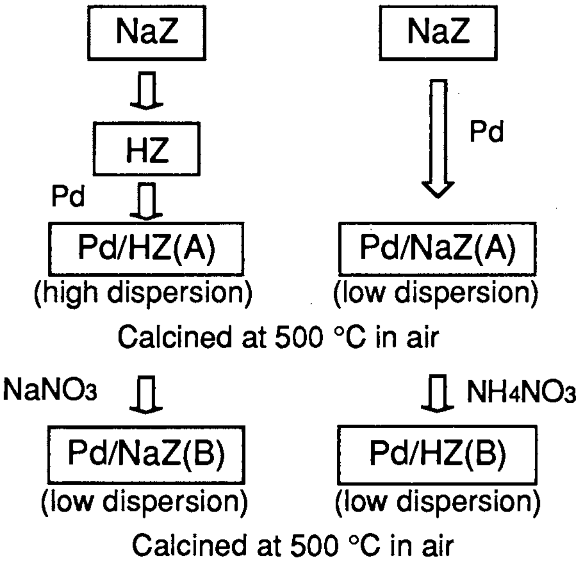

Fig. 1. Preparation of Pd ion-exchanged ZSM-5.

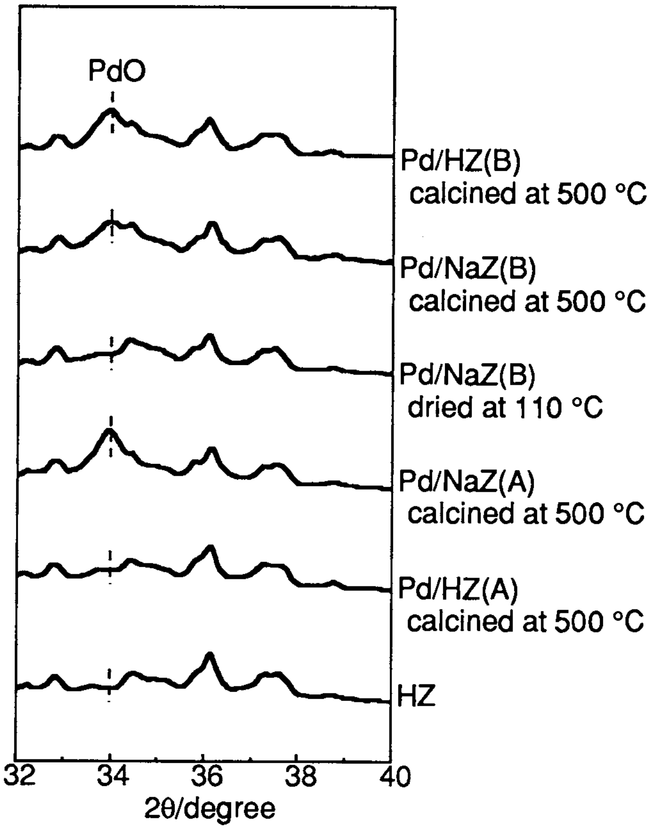

Fig. 2. Powder diffraction patterns of Pd ion-exchanged ZSM-5.

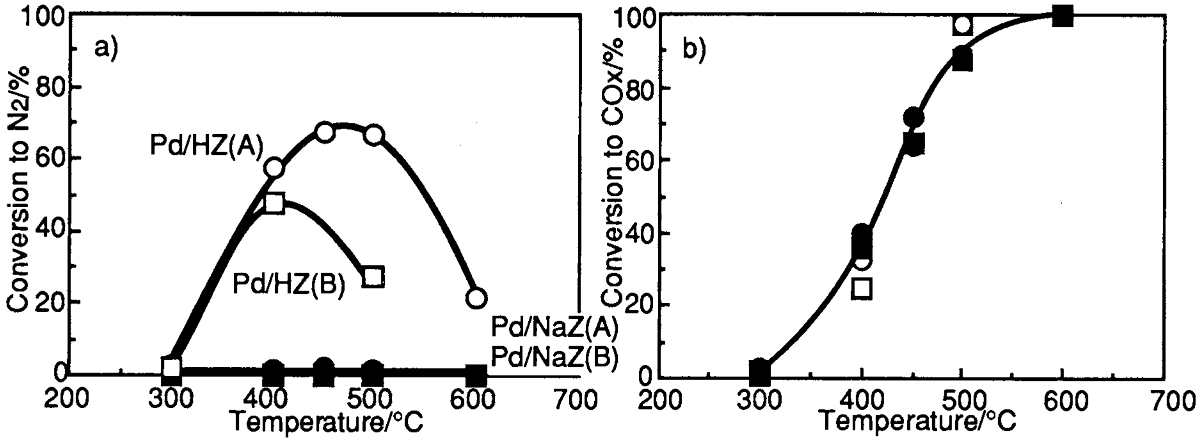

Fig. 3. Reduction of NO by methane over several catalysts as a function of reaction temperature. a) Conversion of NO to N_2. b) Conversion of CH_4 to COx.
○; Pd/H-ZSM-5(A), □; Pd/H-ZSM-5(B), ●; Pd/Na-ZSM-5(A), ■; Pd/Na-ZSM-5(B).
NO; 1000 ppm, CH_4; 2000 ppm, O_2; 2%, catalyst weight; 0.5 g, GHSV; 9000 h^{-1}.

similar.

Figure 3 shows the results of the NO-CH_4-O_2 reaction over these Pd ion-exchanged catalysts. As we reported before,[1)] Pd/HZ(A) showed a high catalytic activity for NO reduction, while Pd/NaZ(A) showed poor results. What is remarkable is that Pd/HZ(B) was as active as Pd/HZ(A) at 400 °C, despite of the low palladium dispersion, although the activity became lower at high temperatures. On the other hand, Pd/NaZ(B) was inactive for the reaction of NO just like Pd/NaZ(A). These results evidently show that the combination of palladium and the protonic form zeolite is essential for the reduction of NO by methane in the presence of oxygen. Although the acidity measurements have not been carried out, it may be reasonable to assume that the protonic acidity of H-ZSM-5 is responsible for the difference. It is also noteworthy that the oxidation of methane was very similar among the four catalysts.

The results of several reactions of NO and NO_2 over Pd/HZ(A) at 400 °C are compared in Fig. 4. Conversion to N_2 in the NO-CH_4 reaction was much lower than that in the NO-CH_4-O_2 reaction, indicating that the presence of O_2 is important for the reduction of NO in the latter reaction. The rates of N_2 formation in the NO_2-CH_4-O_2 and NO_2-CH_4 reactions were significantly higher than the rate in the NO-CH_4-O_2 reaction. These results are similar to those observed for the NO-C_3H_6-O_2 reaction over Ce-ZSM-5,[3)] and indicate that NO is oxidized to NO_2 in the first step and then N_2 is formed in the following reaction between NO_2 and CH_4.

$$NO \xrightarrow{O_2} NO_2 \xrightarrow{CH_4} N_2$$

Next we attempted to clarify in which step of the above scheme the coexistence of the acidity and palladium is necessary. Results are shown in Table 1. As for the oxidation NO to NO_2, the first step, Pd/HZ(A) and Pd/NaZ(A) showed similar activities, so that the difference between the two catalysts in the NO reduction is not due to this step. Actually, the activity for the NO-O_2 reaction decreased by Pd and Na ion-exchange; H-ZSM-5 > Pd/NaZ ~ Pd/HZ > Na-ZSM-5. As for the next step, that is, the NO_2-CH_4 reaction, Pd/HZ was very active for N_2 formation, while Pd/NaZ was almost inactive. The results in Table 1 are those for the (A) series. Similar results were obtained for the (B) series, as well; Pd/HZ(B) was active for NO_2-CH_4 reaction, while Pd/NaZ(B) little active. Thus we may conclude that the coexistence of acidity and palladium is required in the reaction between NO_2 and CH_4.

Both Pd/HZ(A), (B) and Pd/NaZ(A), (B) showed similar high activities for the oxidation of CH_4 in the NO-CH_4-O_2 reaction (Fig. 3 b), and the CH_4-O_2 reactions (Table 1). In contrast, all catalysts without palladium were little active for the oxidation of methane in these two reactions. Therefore, it is probable that the role of Pd is to activate CH_4 to promote the reaction between NO_2 and CH_4.

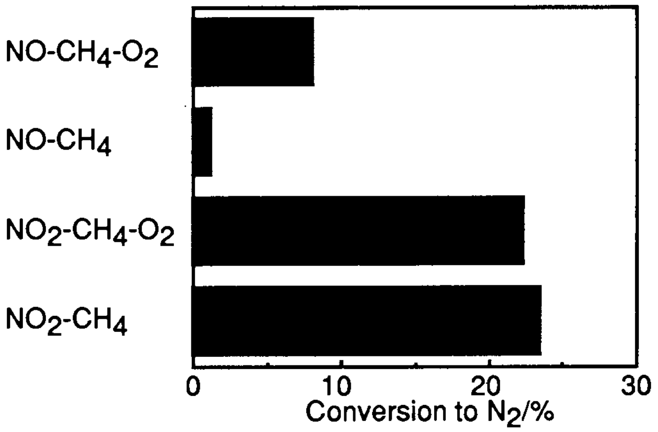

Fig. 4. Catalytic Activities of Pd/H-ZSM-5 for several reactions. Reaction temperature; 400 °C. Catalyst weight; 0.05 g.

Table 1. Activities of Pd/H-ZSM-5, Pd/Na-ZSM-5 and H-ZSM-5 for Several Reactions

Reaction	Conversions to NO_2/%		
	Pd/H-ZSM-5(A)	Pd/Na-ZSM-5(A)	H-ZSM-5
NO-O_2[a)]	11.1	11.5	25.5
	Conversions to N_2 (to COx in parenthesis)/%		
NO-CH_4-O_2[a)]	57.4(32.5)	1.1(35.7)	5.2(1.2)
NO_2-CH_4[b)]	23.5(13.4)	1.0 (2.0)	1.3(0.5)
CH_4-O_2[a)]	- (65.8)	-(59.4)	- (0)

NO(NO_2); 1000 ppm, CH_4; 2000 ppm, O_2; 2%. Catalyst weight; a) 0.5 g, b) 0.05 g. Reaction temperature; 400 °C.

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