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Reduction of nitric oxide with methane on Pd/Co/H-ZSM-5 catalysts: cooperative effects of Pd and Co

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Reduction of low concentration of nitric oxide (NO) with methane as a reductant under wet conditions has been investigated using Pd/Co/H-ZSM-5 catalysts and the effects brought about by coexistence of Pd and Co are discussed. The role of Co is attributed to the acceleration of oxidation of NO to NO_2, which is the necessary species for reduction of NO with CH_4 on Pd sites. A Pd/H-ZSM-5 loading of 1 wt% Co shows a maximum activity for NO reduction as well as for NO oxidation. Excess loading of Co led to a decrease in activity for NO reduction. An XPS study shows that Pd and Co are well dispersed inside the zeolite when the concentrations of Pd and Co are less than 1 wt%. Loading of excess Co, however, causes aggregation of Pd on the surface of ZSM-5.

Keywords: NO reduction; methane; palladium; cobalt; H-ZSM-5 zeolite; cooperative effect

1. Introduction

Many catalysts have been notified to be active for selective catalytic reduction (SCR) of nitrogen oxides with various hydrocarbons under dry conditions [1,2,4–12]. SCR-NO by use of hydrocarbons causes, however, many difficulties in accomplishing practical applications because of demanding reaction conditions in comparison with ordinary catalytic processes. In particular, NOx is contained at an extremely low level of concentration (ppm order), while the concentrations of coexisting oxygen and water vapor, which retard the catalytic reduction of NO, are in the order of percents. Researches have been focused on catalysts having high activity and selectivity even under wet conditions. Although Cu-zeolites show relatively stable activity in the presence of excess oxygen [1,2], sintering of Cu into Cu oxide under wet conditions leads to the deterioration of the catalytic activity of Cu-ZSM-5 [3].

We have demonstrated that reduction of NO with methane selectively proceeds on Ga- and In-loaded H-ZSM-5 catalysts [13]. The catalytic activities of Ga and In/H-ZSM-5, however, were significantly retarded by water vapor. Depression of the catalytic activity of In/H-ZSM-5 by water vapor is mainly caused by retardation of NO oxidation, which is the first stage of SCR-NO with CH_4 occurring on the Lewis acid sites of the zeolite [14]. The addition of precious metals (Pt, Rh, or Ir) onto In/H-ZSM-5 was found to improve the NO conversion even under wet conditions [15]. The role of the precious metals has been attributed to the acceleration of NO oxidation even in the presence of water vapor.

Similarly, other bicomponent catalytic systems have been proposed for SCR-NO with hydrocarbons: Mn_2O_3 physically mixed with Ce-ZSM-5 [16], with Sn-ZSM-5 [17], or with Au/Al_2O_3 [18], $Pd/SiO_2 + Al_2O_3$ [19], and $Pd/SiO_2 + SO_4^{2-}/ZrO_2$ [20]. Another attractive catalyst reported so far is Pd/Co/H-ZSM-5, which shows high catalytic performance for removal of low concentration NOx, even in moist atmosphere [21]. The effect of the coexistence of Pd and Co on ZSM-5 has been investigated in the present work.

2. Experimental

2.1. Catalyst preparation

The catalysts used in this study were prepared according to the description in ref. [21]. Na-ZSM-5 (SiO_2/Al_2O_3 molar ratio of 40.4) was supplied by Tosoh Co. A Pd/H-ZSM-5 catalyst with a 0.4 wt% Pd loading was prepared by the ion-exchange method: NH_4-ZSM-5 was ion-exchanged by stirring in a solution of $Pd(NH_3)_4Cl_2$, adjusted at pH 10 with 7% NH_4OH at room temperature for 2 h, followed by filtration and washing with decationized water. Co/H-ZSM-5 catalysts were prepared by a similar method using a solution of $Co(CH_3COO)_2$ at 80°C for 20 h. Pd/Co/H-ZSM-5 catalysts were obtained by ion-exchanging Co/NH_4-ZSM-5 at pH 10 and room temperature for 2 h using a solution of $Pd(NH_3)_4Cl_2$. The catalysts were dried at 110°C overnight and changed into H-type ZSM-5 by heat treatment prior to reaction. The chemical compositions of the catalysts were determined by means of ICP. A Pd/Co/H-ZSM-5 with 0.4 wt% Pd and 3.3 wt% Co was used as the standard catalyst for kinetic studies.

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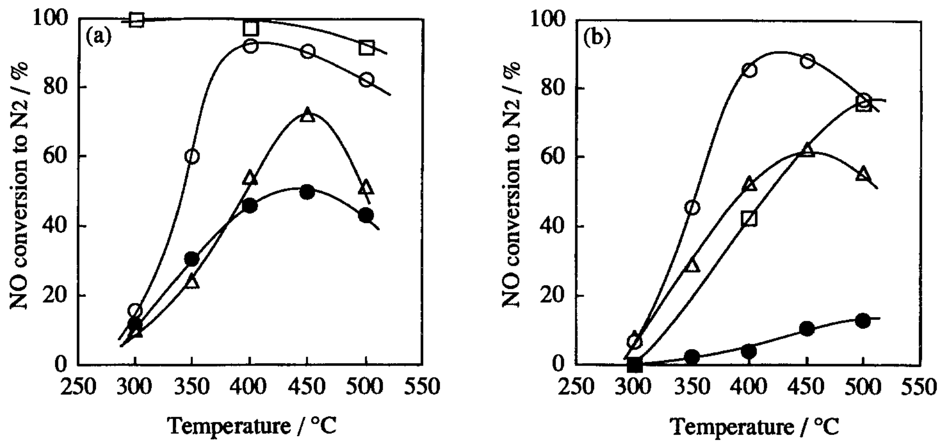

Fig. 1. Catalytic activities of Pd/Co/H-ZSM-5 (○), Pd/H-ZSM-5 (△), Co/H-ZSM-5 (●) and Ir/In/H-ZSM-5 (□) for NO reduction with CH_4 under dry (a) and wet (b) conditions. NO, 100 ppm; CH_4, 2000 ppm; O_2, 10%; H_2O, 0% (a) or 10% (b); total flow rate, 100 cm^3 min^{-1}; catalyst weight, 0.25 g.

2.2. Catalytic activity measurement

Reduction of NOx and oxidation of NO were carried out in a fixed-bed flow reactor, by feeding a mixture of 100–1000 ppm NOx, 0 or 2000 ppm CH_4, 10% O_2, and 10% H_2O, balanced by He, at a rate of 100 cm^3 min^{-1} to 0.1 or 0.25 g catalyst. Kinetic studies employed higher GHSV to obtain low levels of NOx conversion below 30%. Water vapor was admitted by passing He through a saturator heated in a water bath controlled at 60°C, and the wet He was mixed with other reactants. The reactant stream-line was heated at 100°C to avoid H_2O condensation. Catalysts were pretreated in a 20% O_2/He stream at the rate of 5°C/min to 500°C and held at 500°C for 1 h prior to reaction. Effluent gases were analyzed using a gas chromatograph and a chemiluminescence NOx analyzer. Catalytic activities were evaluated by the level of NOx conversion to N_2.

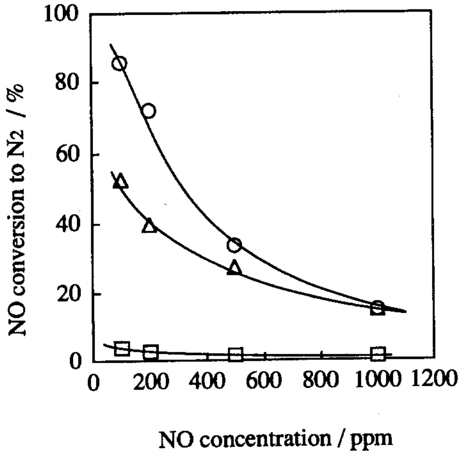

Fig. 2. NO concentration dependence for the activities of NO reduction with CH_4 on Pd/Co/H-ZSM-5 (○), Pd/H-ZSM-5 (△), and Co/H-ZSM-5 (□). NO, 100–1000 ppm; CH_4, 2000 ppm; O_2, 10%; H_2O, 10%; total flow rate, 100 cm^3 min^{-1}; catalyst weight, 0.25 g; reaction temperature, 400°C.

2.3. XPS measurement

The surface states of Pd and Co species were studied by X-ray photoelectron spectroscopy (XPS). For XPS studies, 1 wt% Pd-loaded catalysts were used. Spectra of Pd 3d and Co 2p were recorded with JPS90MX (Jeol). Monochromated Mg Kα radiation (1254 eV) was used for the measurements. The sample was pressed into a disk, set into the XPS sample holder, and outgassed to 7.0×10^{-7} Pa for more than 1 day before each measurement. The 1s level of adventitious carbon (atmospheric hydrocarbons and surface carbon oxides) was taken as the internal reference, with the peak position at 284.6 eV.

3. Results and discussion

Fig. 1 shows the catalytic activities of Pd/H-ZSM-5, Co/H-ZSM-5, and Pd/Co/H-ZSM-5 for the reduction of 100 ppm NO with CH_4 in the absence (a) and presence (b) of H_2O in the reactant feed. As a reference, the activ-

Table 1
Summary of kinetic data for NOx reduction with CH_4 on Pd/Co/H-ZSM-5, Pd/H-ZSM-5 and Co/H-ZSM-5 catalysts

Reaction	Catalyst	Reaction order [a] with respect to			
		NO	NO_2	CH_4	O_2
$NO–CH_4–O_2$	Pd/Co/H-ZSM-5	0.1		1.2	0.0
	Pd/H-ZSM-5	0.6		0.5	0.3
	Co/H-ZSM-5	1.0		0.4	0.0
$NO_2–CH_4$	Pd/Co/H-ZSM-5		0.3	–	
	Pd/H-ZSM-5		0.3	–	

[a] Concentrations: NOx, 50–1500 ppm; CH_4, 500–2000 ppm; O_2, 4–12%. Reaction temperature, 400°C. Catalyst weight: 0.03–0.04 g for Pd/Co/H-ZSM-5; 0.03–0.1 g for Pd/H-ZSM-5; 0.5 g for Co/H-ZSM-5.

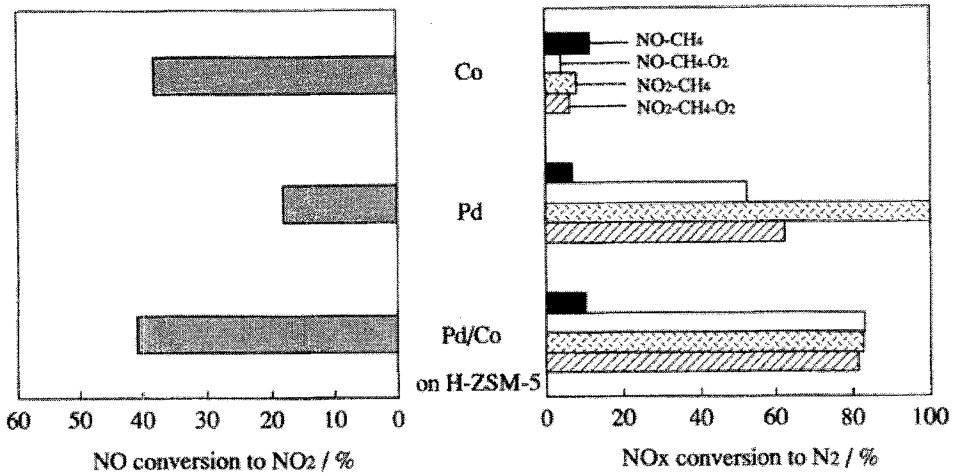

Fig. 3. NOx reduction with CH_4 and NO oxidation on Pd/Co/H-ZSM-5, Pd/H-ZSM-5, and Co/H-ZSM-5 catalysts. NO (or NO_2), 100 ppm; CH_4, 0 or 2000 ppm; O_2, 0 or 10%; H_2O, 10%; total flow rate, 100 cm^3 min^{-1}; catalyst weight, 0.25 g; reaction temperature, 400°C.

ity of the Ir/In/H-ZSM-5 catalyst is also shown, which has high catalytic activity for low-concentration NO reduction in the presence of H_2O [22]. H-ZSM-5 catalysts containing Co [8] and Pd [11] have elsewhere been reported to be active for NO reduction under dry conditions. NO was completely reduced on Ir/In/H-ZSM-5 under these conditions. When the reactant contained 10% of H_2O, however, NO conversion on Ir/In/H-ZSM-5 as well as on Co/H-ZSM-5 decreased significantly in the temperature range of 300–400°C, as shown in fig. 1b. On the other hand, Pd/H-ZSM-5 exhibited high activity in the whole range of temperature. Pd/Co/H-ZSM-5 gives much higher catalytic activity than Pd/H-ZSM-5, indicating that there is a synergistic effect between Pd and Co on H-ZSM-5.

Fig. 2 shows the %conversion of NO to N_2 in the presence of water vapor as a function of NO concentration at the same total flow rate (100 cm^3 min^{-1}). Pd/H-ZSM-5 and Pd/Co/H-ZSM-5 gave a similar level of conversion for a high concentration NO, 1000 ppm. Upon decreasing the NO concentration, the NO conversion increased on both of these catalysts and a higher NO conversion was obtained on Pd/Co/H-ZSM-5 than on Pd/H-ZSM-5. Co/H-ZSM-5 was not so active under these reaction conditions. The orders of reaction rate are summarized in table 1, in which conversions of NO or NO_2 and CH_4 were lower than 30%. It is obvious that the reaction order with respect to NO on Pd/H-ZSM-5 is decreased by the coexistence of Co, which leads to the effectiveness for low concentration NO reduction.

To understand the role of Co sites, a series of NOx reduction and NO oxidation reactions on Co/H-ZSM-5, Pd/H-ZSM-5, and Pd/Co/H-ZSM-5 catalysts were investigated. Typical results are shown in fig. 3. Pd/H-ZSM-5 showed no activity for the NO–CH_4 reaction, while NO was reduced in the presence of oxygen. It is obvious that NO_2 is more reactive than NO, in accordance with the report by Nishizaka and Misono [11]. The decrease in NO_2 conversion by the presence of O_2 on Pd/H-ZSM-5 is attributed to the oxidation of CH_4, leading to the decrease in selectivity for NO_2 reduction with CH_4. Reduction of NOx with CH_4 hardly proceeded on Co/H-ZSM-5 under these experimental conditions, while the activity for NO oxidation was higher than that of Pd/H-ZSM-5. It is interesting to note that the catalytic activity of Pd/Co/H-ZSM-5 for oxidation of NO was comparable to that of Co/H-ZSM-5, and Pd/Co/H-ZSM-5 gave larger NOx conversions in NOx–CH_4–O_2 than Pd/H-ZSM-5. The observed reaction order with respect to NO_2 in the NO_2–CH_4 reaction was the same for Pd/H-ZSM-5 and Pd/Co/H-ZSM-5, as shown in table 1. These results lead us to deduce that formation of NO_2 on Co sites of Pd/Co/H-ZSM-5 is effective for NO

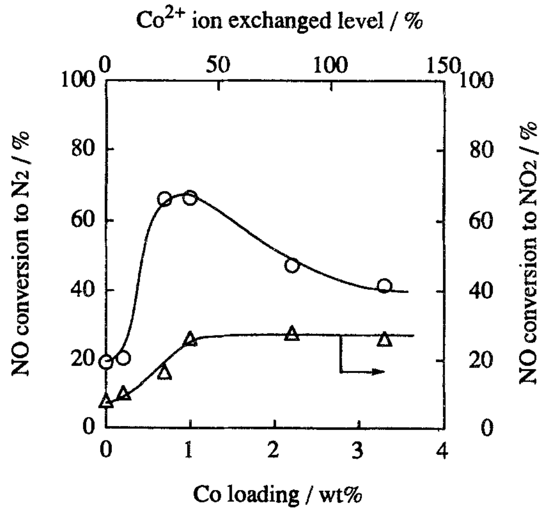

Fig. 4. Effect of Co loading on the catalytic activities of Pd/Co/H-ZSM-5 for NO reduction with CH_4 and NO oxidation. NO–CH_4–O_2 reaction: NO, 100 ppm; CH_4, 2000 ppm; O_2, 10%; H_2O, 10%. NO–O_2 reaction: NO, 100 ppm; O_2, 10%; H_2O, 10%. Total flow rate, 100 cm^3 min^{-1}; catalyst weight, 0.1 g; reaction temperature, 400°C.

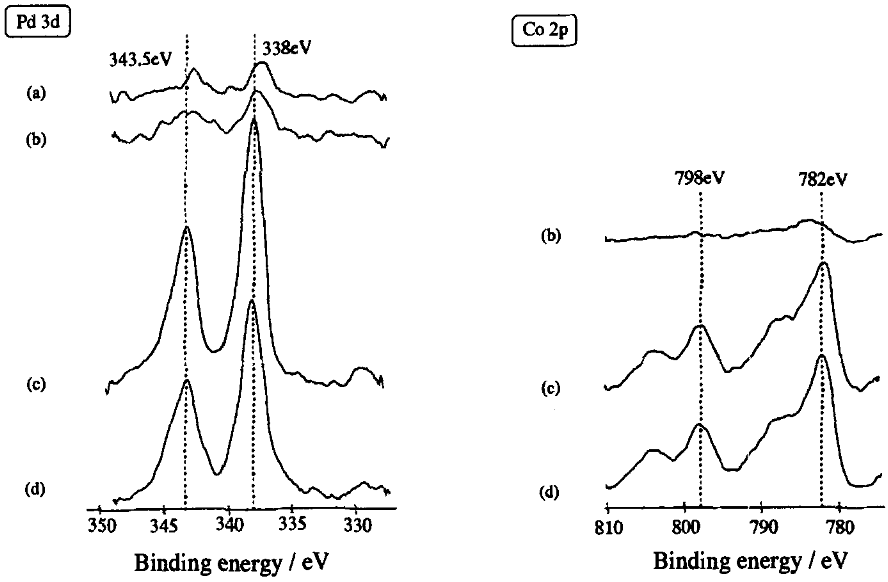

Fig. 5. X-ray photoelectronic spectra of Pd 3d and Co 2p on Pd/H-ZSM-5 and Pd/Co/H-ZSM-5. (a) Pd(1.0 wt%)/H-ZSM-5, (b) Pd(1.0 wt%)/Co(1.0 wt%)/H-ZSM-5, (c) Pd(1.0 wt%)/Co(2.2 wt%)/H-ZSM-5, and (d) Pd(1.0 wt%)/Co(3.3 wt%)/H-ZSM-5.

reduction and that NO is most probably reduced by CH_4 via NO_2 on Pd sites.

Fig. 4 shows the variation in catalytic activities of Pd/Co/H-ZSM-5 for oxidation and reduction of NO as a function of Co content. The upper scale of fig. 4 shows the ion-exchanged level of Co^{2+}. The catalytic activity for NO oxidation increased with increasing Co content up to 1 wt% and then leveled, indicating that less than 1 wt% Co can exist in the appropriate state for NO oxidation. The catalytic activity for NO reduction increased with increasing activity for NO oxidation, and had a maximum at 1 wt% of Co-loaded Pd/H-ZSM-5. When excess Co was loaded, the catalytic activity for NO reduction decreased with increasing conversion of CH_4 by combustion.

The results of XPS observation for the surface states of Co and Pd in Pd/Co/H-ZSM-5 are shown in fig. 5. The content of Pd loaded on each sample was 1 wt%. Pd/H-ZSM-5 gave two peaks at 343.5 and 338 eV, corresponding to Pd $3d_{3/2}$ and $3d_{5/2}$, respectively. When 1 wt% Co coexisted with Pd, the intensities of these peaks were as low as those of Pd/H-ZSM-5. As the content of Co increased to 2.2 and 3.3 wt%, peak intensities increased, showing that Pd particles aggregated onto the surface of ZSM-5. Peaks at 798 and 782 eV, assigned respectively to Co $2p_{1/2}$ and $2p_{3/2}$, were observed on these samples, and their intensities were strengthened on increasing the Co content.

In the procedure of catalyst preparation, Co was firstly ion-exchanged into H-ZSM-5, followed by loading of Pd. If the amount of Co introduced to H-ZSM-5 was small, then Co can be ion-exchanged and Pd can also be ion-exchanged and they are highly dispersed inside Co/H-ZSM-5. Such highly dispersed states of Co and Pd corresponded to high catalytic activities for NO oxidation and reduction. Excess amounts of Co are located on the outer surface of ZSM-5 as cobalt oxides, which might oxidize CH_4 to decrease the selectivity for NO reduction. After introducing excess Co, Pd can hardly be ion-exchanged into H-ZSM-5, and would be loaded as large particles on the surface of the zeolite, as shown by XPS results. The results of the present work seem to show a close relation between the dispersed states of Co and Pd and their catalytic activities for NO oxidation and reduction. The states of Co and Pd, as in accordance with XPS observations, are illustrated in fig. 6. Highly dispersed Co^{2+} and Pd^{2+} in H-ZSM-5 catalyze NO oxidation and reaction between NO_2 and CH_4, respectively. On the contrary, Co and Pd in low-dispersion state, being located on the outer surface of ZSM-5, are less selective for NO oxidation and reduction.

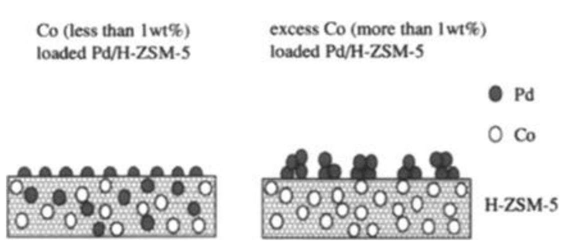

Fig. 6. Cooperative effect of Co on the surface state of Pd on H-ZSM-5.

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