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Co Cation Effects on Activity and Stability of Isolated Pd(II) Cations in Zeolite Matrices for Selective Catalytic Reduction of Nitric Oxide with Methane

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Palladium ion-exchanged zeolites (ZSM-5, mordenite, ferrierite, Y, beta) were tested to evaluate catalytic activity for selective reduction of nitric oxide with methane (CH_4-SCR) and stability in the presence of 10% water vapor at a relatively high temperature of 500°C. Deactivation of the catalytic activity was inevitable on Pd/HZSM-5 with a Si/Al ratio of 19.8 under the reaction conditions. When the Si/Al ratio decreased, the durability was slightly enhanced. Among the zeolites tested, palladium supported on mordenite showed stable NO conversions. The addition of cobalt effectively stabilized the activity of Pd–H-zeolites, particularly with the addition of 3.3 wt% cobalt onto Pd/HZSM-5, of which no deactivation was noticeable for at least 50 h. Isolated Pd^{2+} cations on HZSM-5 were the active and selective sites for CH_4-SCR. The isolated Pd^{2+} cations could not be exchanged by Na^+ cations in NaCl titration test after the addition of 3.3 wt% cobalt, while NH_4NO_3 titration revealed that the isolated Pd^{2+} existed in the sample. This means that Co^{2+} changes the ion-exchange property of the isolated Pd^{2+}, leading to a much higher stability than Pd/HZSM-5 with regard to durability. The effect of Co^{2+} on the stability of the isolated Pd^{2+} cations and their sitings in zeolite cavities is discussed.

Key Words: **CH_4-SCR; Pd/HZSM-5; stability; Pd–Co/HZSM-5, ion-exchange property; isolated Pd^{2+}; NaCl titration; NH_4NO_3 titration.**

INTRODUCTION

Zeolites have prevailed in various catalytic systems since the discovery of a method to produce them synthetically, and the significant amount of subsequent evolution has attracted interest in their structural and catalytic properties. Most zeolite utilization is in their protonic forms as acid catalysts and occurs in the field of petroleum chemistry. Also, ion exchanges of rare-earth elements for hydrothermal stability in the 1960s and of Zn(II) and Ga(III) for aromatization in the 1970s showed additional ways to use zeolite catalysts in the petrochemical industry. Many reactions have achieved high yields by the use of zeolite-supported metal cation catalysts. A recent development by Panov and co-workers regarding the direct synthesis of phenol from benzene using N_2O, catalyzed by Fe cations on zeolites (1), clarified the need for more knowledge about the catalytic properties of metal cations occluded in zeolite cavities. Another well-known reaction catalyzed by metal cations on zeolites is selective catalytic reduction of nitric oxide by the use of hydrocarbons (HC-SCR). To date, Cu (2), Co (3), Ga (4), In (4), and Fe (5) incorporated in zeolite matrices as cations have been found to promote this reaction.

Among numerous metal cations on zeolites or metal oxides that catalyze HC-SCR, zeolite-supported palladium catalysts have garnered much attention (6–14) since they show a high performance for NO reduction by the use of methane as a reducing agent. Palladium on zeolites was first reported by Nishizaka and Misono to show high catalytic activity for CH_4-SCR (6). Loughran and Resasco (7) noted that palladium sites and acid sites are preferably intimate with each other, and that the acidity is needed to transform palladium into a highly dispersed state such as an isolated Pd^{2+} while the palladium on a nonacidic support tends to form a PdO cluster (8). With respect to the redispersion of the palladium species, Adelman and Sachtler reported that the exposure of a reactant mixture of NO_2–CH_4–O_2 provides the reconstruction of the isolated Pd^{2+} species (9). They clearly showed the effect of the acid sites in zeolite on the creation of the active palladium species as follows: $PdO + 2H^+ \rightarrow Pd^{2+} + H_2O$. The stoichiometry for the formation of active sites on Pd-zeolites was also indicated by Bell and co-workers (10), who deduced from the studies of infrared spectroscopy that the palladium active species are stabilized at the pair sites of the next nearest neighboring Al of zeolite, denoted by $Z^-H^+(PdO)H^+Z^-$. Later, they confirmed in their computational studies how the next nearest neighboring Al sites facilitate the stabilization of the

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palladium species (15). Previously, we established that the palladium species on HZSM-5 are located in an isolated state, that is, the isolated Pd^{2+}, as determined by “NaCl titration” (12).

More than one decade has passed since the first report on HC-SCR catalyzed by Cu cations on ZSM-5 was published. Unfortunately, however, this reaction has not yet been realized in practice (16). Zeolite-based catalysts, which are known by their high activities and selectivities, cannot maintain their activities under practical conditions and a stable catalytic activity for a more prolonged period than the conventional experimental conditions is indispensable for practical application. The zeolite-based palladium catalyst is well known to show high activity for CH_4-SCR, even in the presence of water vapor (17), while it shows low durability against H_2O (11, 18). One of the most serious causes for the low durability is the agglomeration of palladium cations into bulky PdO particles outside of the zeolite pore structure, not only by hydrothermal treatment (11) but also even in use under the reaction conditions (18).

In our recent work, we observed a pronounced effect of cobalt species on the durability of Pd–Co/HZSM-5 for CH_4-SCR in the presence of H_2O (18). We evaluated the effect of second components on the catalytic performance of Pd/HZSM-5 zeolite with a durability test of NO reduction with CH_4 at a relatively high temperature of 500°C in the presence of water vapor for a prolonged period, and among the second components tested, Co, Rh, Ag, Ce, and Fe introduced individually to the Pd/HZSM-5 enhanced the durability. In particular the addition of 3.3 wt% cobalt led to a stable NO conversion for more than 40 h in the presence of H_2O. Here we discuss the roles of the cobalt species on the stable performance of Pd–Co/HZSM-5 while making reference to the cations sited in some types of zeolite cavities.

EXPERIMENTAL

Catalysts Preparation

The zeolites used in this work are summarized in Table 1. ZSM-5 with Si/Al ratios 11.9, 19.8, and 35 were supplied by Tosoh Co. Mordenite (MOR) with Si/Al ratio 7.5 and ferrierite (FER) with Si/Al ratio 8.5 were manufactured by Catalysis & Chemicals, Inc., and Tosoh Co., respectively. Faujasite Y with Si/Al ratio 2.8 was supplied by Catalysis & Chemicals, Inc. Zeolite beta (BEA) with Si/Al ratio 15 was synthesized by a steam-assisted crystallization method, which is described in detail elsewhere (19). Palladium catalysts supported on those zeolites were prepared according to the description in our previous work (12). First of all, an NH_4^+-form zeolite was prepared by ion exchange with 1 M NH_4NO_3 aqueous solution. Then, typically, NH_4-ZSM-5 was ion exchanged by stirring in a 0.1 M $Pd(NH_3)_4Cl_2$ solution at room temperature. The chemical composition of catalysts was determined by means of inductively coupled plasma (ICP) atomic emission spectroscopy. The amount of palladium on zeolite was typically fixed at 0.4 wt%. When the palladium loading was changed, the abbreviation as Pd(content: wt%)/H-zeolite was used. A palladium catalyst, in which 0.4 wt% palladium was supported on silica, was also prepared by impregnation of SiO_2 in a 0.1 M $Pd(NO_3)_3$ solution at 80°C. All the catalysts were dried at 110°C overnight, followed by calcination at 500°C in 20% oxygen-containing flow prior to reaction. After the calcination, the catalyst was cooled to the temperature where the catalytic activity test would be carried out. Cobalt onto Pd/HZSM-5 were introduced individually by ion exchanging in a 1 M cobalt acetate solution at 80°C. The loadings of cobalt were at 1, 2.2, 3.3, and

TABLE 1

Zeolite Catalysts Used

Catalyst	Zeolite type	Si/Al molar ratio	Pd (wt%)	Pd/Al molar ratio	Co (wt%)	Co/Al molar ratio
Pd/HZSM-5	MFI	19.8	0.40	0.05	0	—
Pd(1)/HZSM-5	MFI	19.8	1.0	0.12	0	—
Pd(2)/HZSM-5	MFI	19.8	2.0	0.24	0	—
Co(3)/HZSM-5	MFI	19.8	0	—	3.3	0.72
Pd–Co(1)/HZSM-5	MFI	19.8	0.40	0.05	1.0	0.21
Pd–Co(2)/HZSM-5	MFI	19.8	0.40	0.05	2.2	0.48
Pd–Co(3)/HZSM-5	MFI	19.8	0.40	0.05	3.3	0.72
Pd–Co(5)/HZSM-5	MFI	19.8	0.40	0.05	5.2	1.12
Pd/HZSM-5(11.9)	MFI	11.9	0.40	0.03	0	—
Pd–Co(3)/HZSM-5(11.9)	MFI	11.9	0.40	0.03	3.3	0.45
Pd/HZSM-5(35)	MFI	35.0	0.40	0.08	0	—
Pd/HMOR	mordenite	7.5	0.40	0.02	0	—
Pd–Co(3)/HMOR	mordenite	7.5	0.40	0.02	3.3	0.30
Pd/HFER	ferrierite	8.5	0.40	0.02	0	—
Pd/HY	faujasite Y	2.8	0.40	0.01	0	—
Pd/HBEA	beta	15.0	0.40	0.04	0	—

5.2 wt% on H-zeolites, followed by ion exchange of palladium. The content of cobalt loaded on zeolites is denoted in this paper as Pd–Co(content: wt%)/H-zeolite, for example, Pd–Co(3)/HZSM-5 (see Table 1).

Catalytic Activity Test

Reduction of NO was carried out in a fixed-bed flow reactor, by feeding a mixture of 100 ppm NO, 2000 ppm CH_4, 10% O_2, and 0 or 10% H_2O in He balance at a rate of 100 $cm^3\,min^{-1}$ to 0.1-g catalyst at the temperature of 400 or 500°C. Effluent gases were analyzed by means of gas chromatography and chemiluminescence NO_x analysis. Catalytic activities were evaluated by the level of NO conversion to N_2. N_2O was not detected during the activity tests under the conditions used in this study.

NaCl and NH_4NO_3 Titration Methods

Aqueous solutions of NaCl and NH_4NO_3 were used as the media for the ion exchange of palladium species on zeolites. It was found that the isolated Pd^{2+} could be quantitatively exchanged by Na^+ cations in the NaCl solution (12). After the ion exchange, the amounts of cobalt and/or palladium eluted into the filtrate were measured with ICP. The amount of palladium cations from Pd(0.4)/HZSM-5 thus was determined 0.037 mmol/g-zeolite, which coincided well with the whole amount of palladium in this catalyst. Because the exchangeable amount of palladium cations from PdO(0.4)/SiO_2 was negligibly small, it is obvious that the nature of palladium species on HZSM-5 is quite different from that in PdO/SiO_2 in terms of ion-exchange ability. This technique is, therefore, useful to determine the amount of the isolated Pd^{2+} in Pd/HZSM-5 catalysts, and we will hereafter refer to it as "NaCl titration."

The amount of the isolated Pd^{2+} was determined by the method of NaCl or NH_4NO_3 titration using a 0.02 M NaCl or a 1 M NH_4NO_3 aqueous solution. After calcination at 500°C or after the durability test reaction, 30 mg of a palladium-containing sample was stirred in the solution at 80°C for 1 h, filtered, and the concentration of palladium in the filtrate was determined by ICP. No additional Pd^{2+} was observed to be eluted even with a longer period of ion exchange, except for Pd/HMOR. The mass balance of palladium on/out of the catalyst was always confirmed, as reported previously (12). The palladium eluted out of the catalyst was sited as isolated Pd^{2+} species in the ion-exchange sites of the zeolite. The residual palladium on the catalyst was precipitated species, that is, PdO.

X-Ray Photoelectron Spectroscopic Studies

The surface states of palladium species were studied by means of X-ray photoelectron spectroscopy (XPS). Spectra of Pd 3d were recorded with EscaLab 220-I (VG Instruments). Non-monochromated Mg $K\alpha$ radiation (1254 eV) was used for the measurements. The sample was pressed into a thin disk, set into the XPS sample holder, and outgassed below 1.0×10^{-8} Pa before each measurement. The 2p level of silicon, included in every sample, was taken as the internal reference.

^{27}Al-MAS NMR Studies

Al coordination states on the zeolite samples were confirmed by ^{27}Al-MAS NMR, recorded on a JEOL GSX-400 at the frequency of 104 MHz, pulse width of 4.2 μs, recycle time of 5 s, and scanning times of 200. Chemical shifts were referenced to an external standard of $[Al(H_2O)_6]^{3+}$.

RESULTS

Catalytic Performance of Pd/HZSM-5 and the Effect of Cobalt on the Activity and Stability

Figure 1 shows the catalytic performance of Pd/HZSM-5 for CH_4-SCR at 400 and 500°C. Under a dry condition at 500°C, NO conversion on this catalyst was almost unchanged over 20 h. It showed high catalytic activity and stability at 400°C even in the presence of H_2O. On the contrary, the catalytic activity decreased with time onstream at 500°C under wet conditions, resulting in a very low level of NO conversion after 7 h. The decreased catalytic activity could not be recovered at all by removal of H_2O from the reactant stream, whereas the level of CH_4 conversion was recovered to the level attained in the dry condition, meaning that the selectivity of CH_4 toward NO reduction was lowered by the deactivation.

We described in our previous reports (17, 18) the promotive effects of cobalt on the catalytic activity of Pd/HZSM-5 and on its durability in the presence of H_2O. As shown in Fig. 2, Co-loaded Pd/HZSM-5 showed high stability in

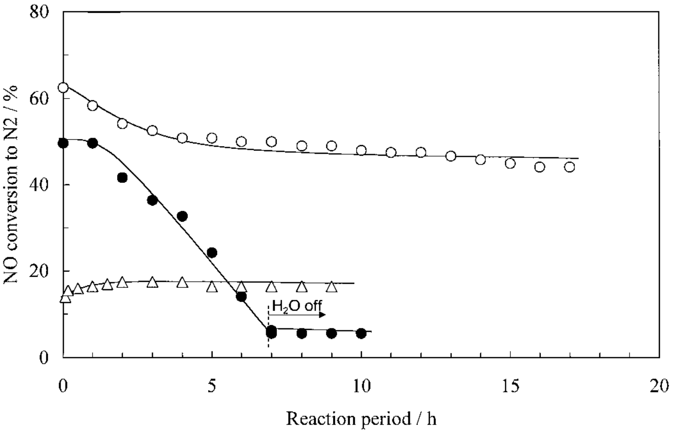


FIG. 1. Effect of H_2O on the catalytic activity of Pd/HZSM-5 for CH_4-SCR: NO, 100 ppm; CH_4, 2000 ppm; O_2, 10%; total flow rate, 100 cm^3/min in the absence (○) or in the presence of 10% H_2O (●, △); catalyst weight, 0.1 g; reaction temperature, 400°C (△), 500°C (○, ●).

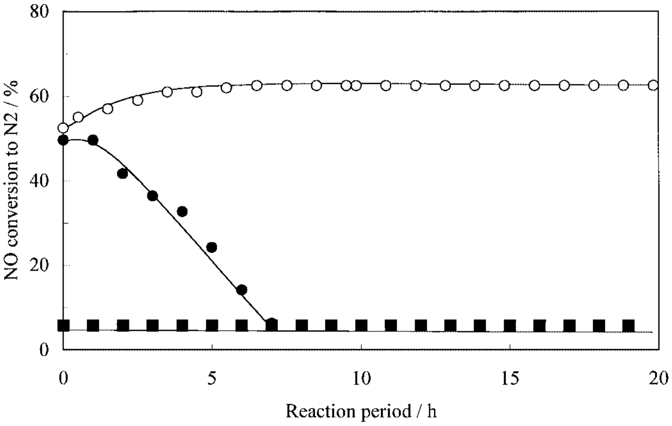


FIG. 2. Durability of (●) Pd/HZSM-5, (■) Co(3)/HZSM-5, and (○) Pd–Co(3)/HZSM-5 for CH_4-SCR under wet conditions: NO, 100 ppm; CH_4, 2000 ppm; O_2, 10%; total flow rate, 100 cm^3/min in the presence of 10% H_2O; catalyst weight, 0.1 g; reaction temperature, 500°C.

the durability test, while cobalt that was ion-exchanged on HZSM-5 hardly showed NO conversion under the same experimental conditions.

The stability effect strongly depended on the loading amount of cobalt, a typical example of which is illustrated in Fig. 3. The initial activity for NO reduction increased by loading Co(1) and then decreased with increasing cobalt content. We found that almost no palladium was loaded on the Pd–Co(5)/HZSM-5, suggesting that no ion-exchangeable sites remained in Co(5)/HZSM-5, of which the Co/Al ratio corresponded to 1.12. Deactivation of these catalysts was suppressed as the amount of cobalt increased, and the activity of Pd–Co(3)/HZSM-5 changed little during the durability test over 50 h. It is interesting to note that the order in the ion exchanges of Co^{2+} up to 3.3 wt% and Pd^{2+} never changed the catalytic activity or stability, that is, Co(3)–Pd/HZSM-5 and Pd–Co(3)/HZSM-5 showed similar NO conversion over the prolonged period of reaction.

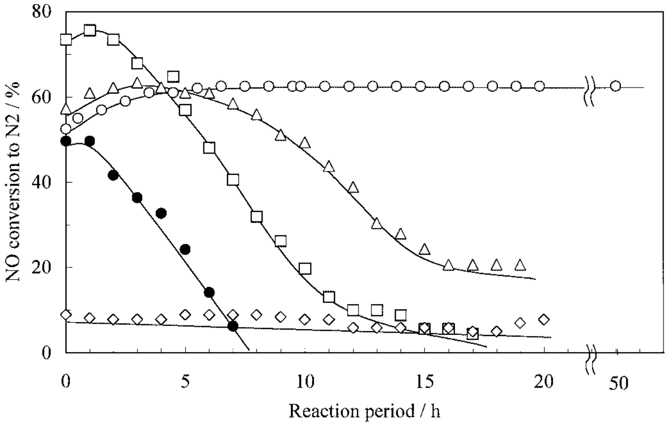


FIG. 3. Effect of cobalt on the catalytic performance of Pd/HZSM-5 for CH_4-SCR under durability test conditions: (●) Pd/HZSM-5, (□) Pd–Co(1)/HZSM-5, (△) Pd–Co(2)/HZSM-5, (○) Pd–Co(3)/HZSM-5, (◇) Pd–Co(5)/HZSM-5; NO, 100 ppm; CH_4, 2000 ppm; O_2, 10%; total flow rate, 100 cm^3/min in the presence of 10% H_2O; catalyst weight, 0.1 g; reaction temperature, 500°C.

Qualitative and Quantitative Analyses of Pd(II) Species on Pd/HZSM-5 and Pd–Co/HZSM-5

NaCl titration, that is, an ion exchange of an isolated Pd^{2+} in Pd/HZSM-5 by use of Na^+ in the aqueous solution of NaCl, was found to effectively determine the amount of isolated Pd^{2+} cations (12). The amounts of the isolated Pd^{2+} thus determined before utilization in the durability test are summarized in Table 2. As shown previously (12), palladium species in Pd/HZSM-5 were located entirely in the cavities of HZSM-5 zeolite as isolated Pd^{2+} cations when the palladium content was below 1 wt% and the Si/Al ratio of HZSM-5 was 19.8. Pd/HZSM-5 used in this study also contained all of the palladium species as isolated Pd^{2+} cations. The addition of cobalt up to 1 wt% did not affect the number of isolated Pd^{2+} cations. The number of isolated Pd^{2+} cations, however, decreased with an increase in cobalt content for Pd–Co(2)/HZSM-5 and Pd–Co(3)/HZSM-5, and almost no isolated Pd^{2+} cations were exchanged by Na^+ in the NaCl titration from Pd–Co(3)/HZSM-5, even after the prolonged period of titration for 24 h at 80°C.

Figure 4 shows the XPS spectra of Pd 3d for Pd/HZSM-5 and Pd–Co/HZSM-5 and for PdO on SiO_2. The values of the binding energy corresponding to the Pd $3d_{5/2}$ on each sample are summarized in Table 3. The absence of a spectrum in the Pd(0.4)/HZSM-5 sample indicates that palladium species on the sample are well dispersed and never located as an aggregated state on the zeolite surface. A moderate spectrum was detected after reaction at 400°C in the presence of water vapor. Pd(1)/HZSM-5 also showed a spectrum with an intensity similar to that of Pd(0.4)/HZSM-5 after use in the reaction. The dispersed state of palladium species at 0.4 wt% was slightly influenced by the addition of 1 wt% cobalt on HZSM-5, and a spectrum could

TABLE 2

NaCl Titration of Pd/HZSM-5 and Pd–Co/HZSM-5

Catalyst	Pd^{2+} (mmol/g)	Co^{2+} (mmol/g)	Pd^{2+}/Pd molar ratio[a]	Co^{2+}/Co molar ratio[b]
Pd(0.4)/HZSM-5	0.037	—	0.98	—
Pd(1)/HZSM-5	0.082	—	0.87	—
Pd(2)/HZSM-5	0.082	—	0.44	—
Pd–Co(1)/HZSM-5	0.032	0.011	0.85	0.06
Pd–Co(2)/HZSM-5	0.004	0.042	0.11	0.11
Pd–Co(3)/HZSM-5	0.002	0.083	0.04	0.15

[a] The value is the molar ratio of Pd^{2+} eluted into NaCl solution per total Pd in the catalyst.

[b] The value is the molar ratio of Co^{2+} eluted into NaCl solution per total Co in the catalyst.

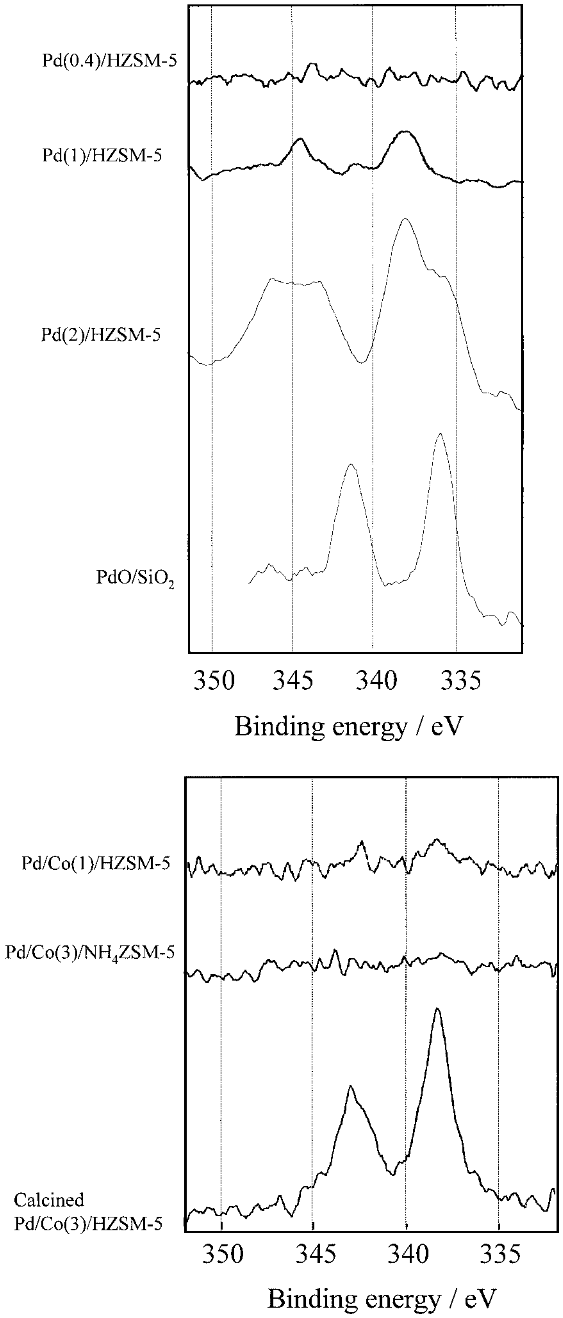


FIG. 4. XP spectra of Pd 3d on Pd/HZSM-5, Pd–Co/HZSM-5, and PdO/SiO_2.

be detected. In contrast, intense peaks were detected on Pd(2)/HZSM-5 and Pd–Co(3)/HZSM-5, indicating that divalent palladium species on the sample were concentrated on the surface or near the pore mouth of ZSM-5 zeolite. We deduced previously (17) that excess loading of cobalt leads to the agglomeration of the divalent palladium species on the outer surface of zeolite. Also, PdO/SiO_2 had surface divalent palladium species, although the binding energy of the divalent palladium species differed from that of the zeolites.

TABLE 3

X-Ray Photoelectron Spectra of Pd $3d_{5/2}$ on Pd/HZSM-5, Pd–Co/HZSM-5, and PdO/SiO_2

Catalyst	Binding energy of Pd $3d_{5/2}$ (eV)			
Pd(0.4)/HZSM-5		—		
After reaction[a]		337.3		
Pd(2)/HZSM-5		337.1	336.4	
Pd–Co(1)/HZSM-5	338.3			
Pd–Co(3)/HZSM-5	338.5			
After reaction[b]	338.1			
$PdO(Pd:0.4)/SiO_2$			336.4	
After reaction[a]			336.3	334.4

[a] $NO–CH_4–O_2$ reaction in the absence of H_2O at 400°C.
[b] $NO–CH_4–O_2$ reaction in the presence of H_2O at 500°C.

Palladium has covalent bonds with oxygen atoms in the oxide, so that a higher level of binding energy corresponds to a more cationic state of palladium; therefore, the divalent palladium species on the zeolite maintains a cationic state like that of the isolated Pd^{2+} even on Pd–Co(3)/HZSM-5. It should be noted that the intense peaks were obtained only after calcination and that the divalent palladium species on $Pd–Co(3)/NH_4ZSM-5$, before calcination, were similar to those on Pd/HZSM-5.

The palladium species in Pd–Co(3)/HZSM-5 were also found to be isolated Pd^{2+} by means of the ion exchange with NH_4^+ called "NH_4NO_3 titration" in this work. The titration results are summarized in Table 4. First, the exchangeabilities of palladium species with Na^+ and NH_4^+ were compared by the use of aqueous NaCl and NH_4NO_3 solutions, respectively. Pd(2)/HZSM-5 was used as a reference, since palladium species on this sample were confirmed by NaCl titration to exist in both states as isolated Pd^{2+} and a precipitated PdO, as shown in Table 2. The amounts of the isolated Pd^{2+} exchanged by Na^+ and NH_4^+ cations are comparable, and, therefore, it is confirmed that only the isolated Pd^{2+} cations on ion-exchangeable sites in zeolite are eluted by means of these titration methods. As obviously shown in Table 4, almost all the palladium species in Pd(0.4)–Co/HZSM-5 catalyst could be exchanged by NH_4^+ cations, irrespective of cobalt content. This means that Pd(0.4)–Co/HZSM-5

TABLE 4

NH_4NO_3 Titration of Pd/HZSM-5 and Pd–Co/HZSM-5

Catalyst	Pd^{2+} (mmol/g)	Co^{2+} (mmol/g)	Pd^{2+}/Pd molar ratio	Co^{2+}/Co molar ratio
Pd(0.4)/HZSM-5	0.033	—	0.88	—
Pd(2)/HZSM-5	0.068	—	0.36	—
Pd–Co(1)/HZSM-5	0.032	0.011	0.85	0.06
Pd–Co(2)/HZSM-5	0.034	0.159	0.91	0.43
Pd–Co(3)/HZSM-5	0.037	0.356	0.99	0.64

contains every palladium as the isolated Pd^{2+} cation in the matrix of Co/HZSM-5. Comparing Tables 2 and 4 also shows that cobalt species were rarely exchanged with Na^+, while NH_4^+ was able to exchange with isolated Co^{2+} cations in zeolite. The amount of Co^{2+} revealed by NH_4NO_3 titration was 0.64 Co^{2+}/Co in Pd–Co(3)/HZSM-5. This means $Co^{2+}/Al = 0.46$, indicating that the cobalt species exists as isolated Co^{2+} cations in the ion-exchange sites of zeolite. The residual cobalt species were considered to be precipitated cobalt oxide.

To understand the role of cobalt species on the stabilization of the isolated Pd^{2+} active for CH_4-SCR, the NH_4NO_3 titration was carried out on the samples after the durability test. Table 5 compares the amounts of isolated Pd^{2+} and Co^{2+} sustainable after the reaction, as shown in Fig. 3. Deactivated catalysts such as Pd/HZSM-5, Pd–Co(1)/HZSM-5, and Pd–Co(2)/HZSM-5 held fewer isolated Pd^{2+} cations than the fresh ones. Interestingly, the amount of isolated Co^{2+} cations also decreased in those samples after the durability test. In contrast, Pd–Co(3)/HZSM-5 possessed the isolated Pd^{2+} as well as Co^{2+} in amounts similar to that of the fresh catalyst.

Palladium (0.4 wt%) was loaded onto Co/HZSM-5 which had been prepared after ion exchange of Co(3)/HZSM-5 with NH_4NO_3, and the subsequently prepared Pd–Co/HZSM-5 was tested in the durability test. The activity of this catalyst was as high as that of Pd–Co(3)/HZSM-5 in the initial period of reaction, while the activity decreased much faster than that of the Pd–Co(3)/HZSM-5. These results suggest that isolated Co^{2+} cations removed from Co(3)/HZSM-5 by NH_4^+ before loading of Pd^{2+} play an important role in the stabilization of the isolated Pd^{2+} on ZSM-5.

Effect of Zeolite Type on the Activity and Stability of Pd(II) Species

Figure 5 compares the catalytic activities of palladium supported on HMOR, HFER, HY, and HBEA zeolites, and Table 6 summarizes the amounts of isolated Pd^{2+} cations in these Pd-zeolites, determined by the NaCl titration. Under the conditions used in the durability test, palladium supported on HFER, HY, and HBEA showed no catalytic activity for CH_4-SCR, even after 10 min of reaction, while only Pd/HMOR catalyzed this reaction. Interestingly, the catalytic activity of Pd/HMOR increased during the initial period of the activity test, and after 10 h a stable NO conversion was given. Ohtsuka and Tabata reported that Pd/MOR showed a higher stability at 450°C than Pd/ZSM-5, but the conversion gradually decreased in their catalytic test in the presence of water vapor (14). In our observation at 500°C, however, no decline in the conversion was seen. It should be noted that a longer time of 3 h was taken to titrate the isolated Pd^{2+} completely in Pd/HMOR (see Table 6); on the other samples 1 h at 80°C was enough to achieve ion-exchange equilibrium of Na^+ in zeolites.

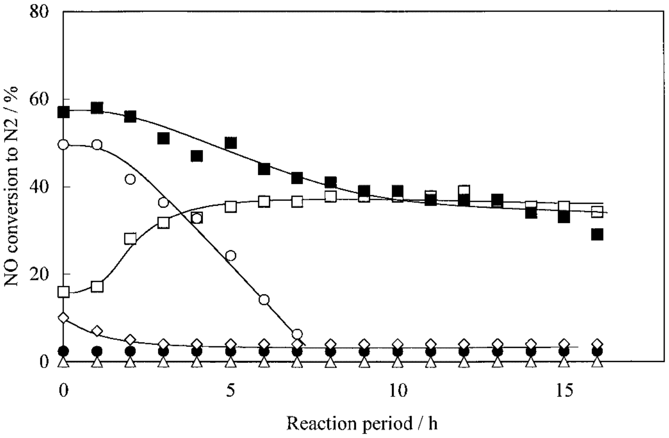


FIG. 5. Effect of zeolite type on the catalytic activity and durability of isolated Pd^{2+} for CH_4-SCR: (○) Pd/HZSM-5, (□) Pd/HMOR, (◇) Pd/HFER, (△) Pd/HBEA, (●) Pd/HY, (■) Pd–Co(3)/HMOR; NO, 100 ppm; CH_4, 2000 ppm; O_2, 10%; total flow rate, 100 cm^3/min in the presence of 10% H_2O; catalyst weight, 0.1 g; reaction temperature, 500°C.

The catalytic performance of Co-loaded Pd/HMOR was also included in Fig. 5. Interestingly, a higher NO conversion than that for Pd/HMOR was kept stable from the beginning of the durability test up to 20 h. As in the case of Pd–Co(3)/HZSM-5, the amount of the isolated Pd^{2+} on HMOR, determined by NaCl titration, decreased with the addition of cobalt (see Table 6) and the NH_4NO_3 titration revealed that the palladium species was entirely isolated Pd^{2+}. It seems that the stabilization effect of the

TABLE 5

Pd^{2+}/Pd Determined by NaCl and NH_4NO_3 Titrations for Pd/HZSM-5 and Pd–Co/HZSM-5: Effect of Reaction

	NaCl titration		NH_4NO_3 titration	
Catalyst	Before reaction	After reaction	Before reaction	After reaction
Pd/HZSM-5	0.98	0.24	0.88	0.68
Pd–Co(1)/HZSM-5	0.85	0.52	0.85	0.76
Pd–Co(2)/HZSM-5	0.11	0.54	0.91	0.52
Pd–Co(3)/HZSM-5	0.04	0.01	0.99	1

TABLE 6

Pd^{2+}/Pd Determined by NaCl Titration for Pd/H-zeolites and Pd–Co/HMOR

Catalyst	Pd^{2+}/Pd molar ratio
Pd/HMOR	0.59 (1)[a]
Pd/HFER	0.50
Pd/HY	0.81
Pd/Hbeta	0.40
Pd/Co(3)/HMOR	0.12 (1)[b]

[a] Pd^{2+}/Pd became 1 after titration for 3 h.

[b] Pd^{2+}/Pd became 1 by NH_4NO_3 titration for 1 h.

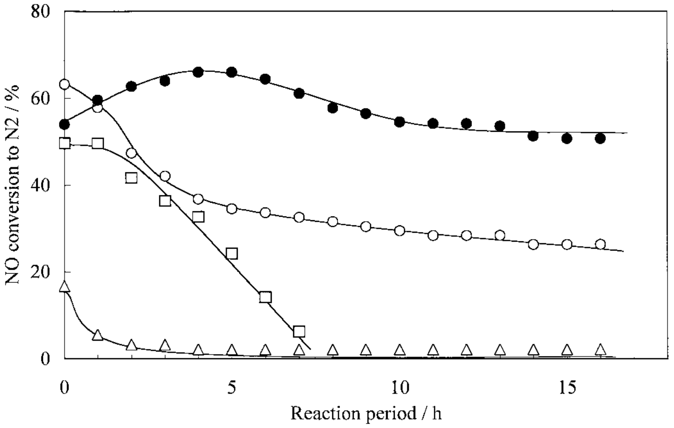


FIG. 6. Effect of Si/Al ratio in ZSM-5 for the catalytic activity and durability of isolated Pd^{2+} for CH_4-SCR: Si/Al ratio: (○) 11.9, (□) 19.8, (△) 35; (●) Pd–Co(3)/HZSM-5 (11.9); NO, 100 ppm; CH_4, 2000 ppm; O_2, 10%; total flow rate, 100 cm^3/min in the presence of 10% H_2O; catalyst weight, 0.1 g; reaction temperature, 500°C.

isolated Pd^{2+} by isolated Co^{2+} can work in different zeolite cavities.

Pd/HFER and Pd/HBEA were also inactive for CH_4 combustion. All of the catalysts used in this study contained isolated Pd^{2+}, as confirmed by NaCl titration, and seen in Table 6, along with precipitated PdO. Palladium supported on zeolite Y has been reported to be inactive for CH_4-SCR by many researchers. Also, in our experiments, Pd/HY was inactive for the reaction even though it contained isolated Pd^{2+}, but on the other hand, it was active for CH_4 combustion. From these results, it appears that the activities of the isolated Pd^{2+} and precipitated PdO for CH_4-SCR and CH_4 combustion are affected by their location surrounded by zeolitic aluminosilicate framework.

Effect of Si/Al Ratio in ZSM-5 Framework on the Stability of Pd(II) Species

The catalytic activities of palladium supported on HZSM-5 with different Si/Al ratios in the framework were evaluated by the durability test of CH_4-SCR, as illustrated in Fig. 6. The activity and selectivity against combustion (not shown) increased with the decrease in Si/Al ratio in the ZSM-5 framework. Also, the stability of isolated Pd^{2+} increased with decreasing Si/Al ratio. The catalytic performance of Co-loaded Pd/HZSM-5 with a Si/Al ratio of 11.9 was also included in this figure. A higher and more stable NO conversion than Pd/HZSM-5(11.9) up to 20 h was given by the addition of Co(3). In this catalyst, also, the amount of the isolated Pd^{2+} decreased in response to cobalt addition, and NH_4^+ titration revealed that the palladium species was entirely the isolated Pd^{2+} (results are not shown). From these results, we concluded that not only the amount of the isolated Pd^{2+} cations but also their stability correlates with the Si/Al ratio of ZSM-5 framework. In contrast, the stabilization effect of isolated Co^{2+} on the catalytic activity of the isolated Pd^{2+} was also observed in ZSM-5 cavities, even though the Si/Al ratio of the framework was changed.

Figure 7 shows MAS NMR spectra of Al on Pd/HZSM-5 and Co(3)–Pd/HZSM-5 with Si/Al ratio of 19.8 before and after durability tests. Al in octahedral coordination was not found in either of the fresh catalysts. Although not so much of the extra-framework Al could be observed on Pd/HZSM-5 after the test, none was observed on Co(3)/Pd/HZSM-5. This indicates that Si/Al ratio is hardly changed during the reaction, and that the irreversible loss

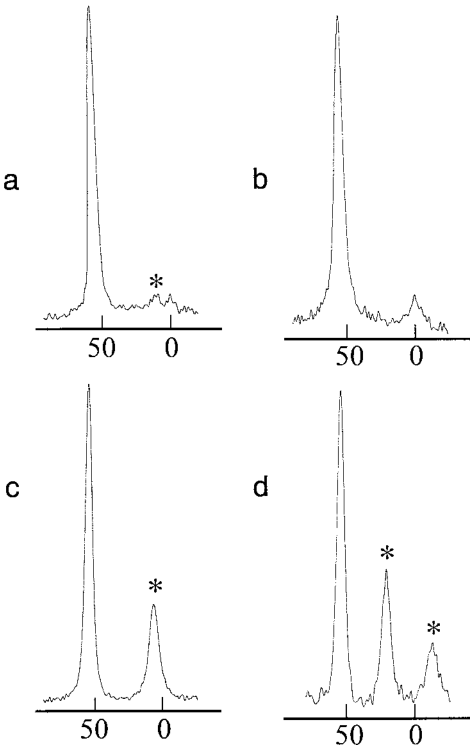


FIG. 7. ^{27}Al-MAS NMR spectra for Pd/HZSM-5 (a, b) and Pd–Co(3)/HZSM-5 (c, d) after reaction at 500°C in the absence (a, c) or in the presence (b, d) of water vapor. Asterisk represents the spinning sideband.

of catalytic activity of Pd/HZSM-5 is mainly due to the formation of extra-framework PdO species.

DISCUSSION

Roles of Cobalt on the Stability of Isolated Pd(II) in Zeolite Cavities

Considering the results obtained in this work, we speculate that the cobalt included in Pd/H-zeolites will (1) enhance zeolites' acidity to stabilize the isolated Pd^{2+}; (2) minimize the residual ion-exchangeable sites so the zeolite framework will not collapse, as discussed in the case of Fe/ZSM-5 (5); and (3) suppress the dealumination from the zeolites' framework to maintain ion-exchange sites for the isolated Pd^{2+}.

For acidity, one can expect this degree of enhancement based on the promotive effect brought about by HMOR having a higher acid strength than HZSM-5 and other zeolites used in this study. However, NH_3-TPD revealed that isolated Co^{2+} cations ion-exchanged in zeolites never changed the acid strength of zeolites, while the acid amount decreased.

Armor and Farris suggested in their report (20) that cobalt-ion-exchanged ZSM-5 following treatment under hydrothermal conditions maintains the same high surface area as it had before the treatment. A not-so-significant decrease in the acid amount of zeolites determined by the NH_3-TPD studies could be observed after the durability tests for over 20 h even on Pd/HZSM-5. Additionally, Pd–Co(3)/HMOR and Pd–Co(3)/HZSM-5 with Si/Al ratios of 7.5 and 11.9, respectively, had many more acid sites but showed stable activities during 20 h. Therefore, the residual acid sites did not so significantly influence the durability of zeolite. Certainly, the addition of cobalt led to the decrease of octahedral aluminum species after the durability test, as qualitatively confirmed by ^{27}Al-MAS NMR, shown in Fig. 7. A more plausible deduction from the NMR study was that cobalt affected the magnetic field of zeolites and Co-loaded zeolite samples gave disordered spectra. As revealed in the durability tests and the NH_4NO_3 titration studies, isolated Co^{2+} is the effective species for stabilizing the isolated Pd^{2+} in the zeolite cavities. The isolated Co^{2+} has unpaired electrons and thus shows a paramagnetic character, resulting in a highly active species for ESR (21). The isolated Pd^{2+} is also affected by co-cations from the viewpoint of the stability against redox treatments (22). Therefore, isolated Co^{2+} cations might change an electronic density within a local range of zeolite cavities.

This phenomenon reminds us of the results obtained by the XPS studies in which the Pd 3d spectrum on 3.3 wt% Co-loaded Pd/HZSM-5 was shifted to a higher level of binding energy. The NH_4NO_3 titration indicates that all of the palladium species on Pd/HZSM-5 and even on Pd–Co(3)/HZSM-5 were located as the isolated Pd^{2+} in the ion-exchange sites of the zeolite. Binding energy of metal, which is measured by XPS, is sometimes shifted to a lower level when the size of the metal is changed. In our case, however, the palladium species on zeolites is the same (isolated Pd^{2+}) and never influenced in size. Therefore, the XPS results obtained in this study indicate that divalent palladium species on Co(3)/HZSM-5 are in a more cationic state than not only covalently bonding PdO but also the divalent palladium species on HZSM-5. The divalent palladium species on Pd–Co(3)/HZSM-5 were stabilized and could maintain their electronic state after the durability test, while some portion of those on HZSM-5 were lowered in the binding energy even after the reaction at 400°C. This corresponds to the characteristic mobility of an isolated Pd^{2+} in zeolite cages as a hydrated cation, leading to the formation of PdO observed after hydrothermal treatments or observed on deactivated samples (11). The changes in selectivity for CH_4-SCR strongly support the fact that the isolated Pd^{2+} sites active for SCR are agglomerated into PdO, which shows CH_4 combustion activity. Because CH_4 conversion on the Pd–Co(3)/HZSM-5 was unchanged, and then the selectivity was also unchanged during the test, we note that this stable performance is not due to a change in the nature of the active site, such as forming a pair site of $[Pd^{2+}–O–Co^{2+}]^{2+}$, but rather to the high stability of the isolated Pd^{2+} active sites.

The enhancement in the stability of the isolated Pd^{2+} by isolated Co^{2+} cations can be judged by the change in ion-exchange property. Thermodynamic affinities of monovalent cations for the ion exchange into ZSM-5 were determined and reported in the literature (23) having the following sequence: $Cs^+ > Rb^+ > NH_4^+ > H_3O^+ > K^+ > Na^+ > Li^+$. A physical retardation of ion exchange cannot be taken into account when one considers the sizes of ZSM-5 cavity and cations and that the titration period used (1 h at 80°C) was long enough to reach ion-exchange equilibrium. Until now, the results have not yet led us to conclude that a "site-selective" extraction of the isolated Pd^{2+} from zeolites occurs during titration. Therefore, the change in the ion-exchange property of the isolated Pd^{2+} by the addition of isolated Co^{2+} cations is the change in thermodynamic affinity onto ZSM-5: the difficulty of ion exchange with Na^+ was diminished by using NH_4^+, which exhibits stronger affinity to exchange in ZSM-5.

It can be concluded that the isolated Co^{2+} species improve the stability of the isolated Pd^{2+} cations in the ion-exchange sites of zeolite by enhancing thermodynamic affinity of the isolated Pd^{2+} to the zeolite framework, resulting in higher catalytic activity and stability for CH_4-SCR under wet and thermal conditions.

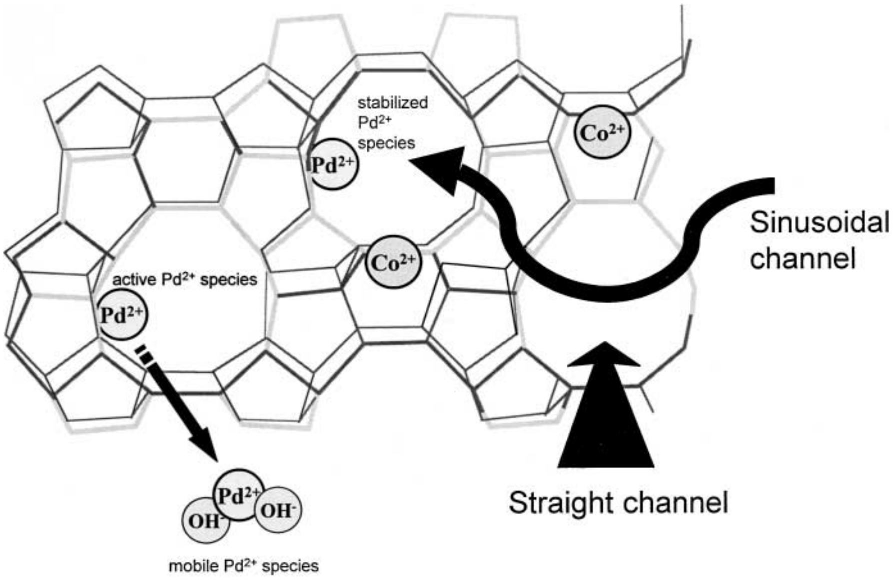
Pd(II) and Co(II) Sitings in Zeolite Cavities

Mortier suggested that divalent cations such as Ca^{2+} and Ba^{2+} are likely to coordinate to six- or eight-membered rings (MR), not to pentasil ones. (24). Wichterlova and co-workers suggested in their recent reports (25–30) that ZSM-5 has three kinds of ion-exchangeable sites for isolated Co^{2+}, the α, β, and γ sites in 6MR, which are located at the straight channel, the channels' intersection, and the sinusoidal channel of ZSM-5, respectively, and that the site selectivity changes by changing the loading amount of cobalt. In this study, the isolated Co^{2+}, exchangeable with NH_4^+, is effective for stabilizing the isolated Pd^{2+}; therefore, isolated Pd^{2+} and Co^{2+} sitings in ZSM-5 cavities were discussed according to the results already reported in the literature.

The Co/Al ratio in Pd–Co(3)/HZSM-5 is 0.72, and the Co^{2+}/Co ratio determined by NH_4NO_3 titration was ca. 0.5; therefore, $Co^{2+}/Al = 0.36$. Co^{2+} cation is primarily located at β sites in ZSM-5 when a small amount of cobalt is loaded, and then α sites with gradual increase of Co^{2+}. Considering the Co^{2+}/Al ratio of 0.36 in Pd–Co(3)/HZSM-5, the isolated Co^{2+} is thought to be located on both α and β sites, according to the literature (28, 29). When loading lesser amounts of cobalt, the isolated Co^{2+} is located only on β sites.

According to Mortier's (24) and Takaishi's rule (31), divalent cations are to be located at the sites in 6MR. The α site is the most released 6MR site among the three kinds of sites in ZSM-5, so when $Pd(NH_3)_4^{2+}$ is ion-exchanged, such a bulky amine complex will be first located in the α site. In comparison to the ion-exchange properties of isolated Co^{2+} and Pd^{2+} in ZSM-5, Co^{2+} has much more affinity for the ion exchange sites than Pd^{2+}. When enough isolated Co^{2+} cations coexist in ZSM-5 along with $Pd(NH_3)_4^{2+}$ to be located in α sites, the isolated Co^{2+} must be placed in the α site to retard stabilization of the isolated Pd^{2+} in the same site. The results observed by the XPS that divalent palladium spectrum on Pd–Co(3)/HZSM-5 appeared after calcination can be explained by the ion exchange, which occurs during calcination to compete for α sites. Therefore, the isolated Pd^{2+} in Pd–Co(3)/HZSM-5 must be located next to the α-siting Co^{2+}, as illustrated in Fig. 8. By being in the closest location to the isolated Pd^{2+}, the isolated Co^{2+} can act as a stabilizer of the isolated Pd^{2+} in zeolite cavities.

A similar interaction between isolated Pd^{2+} and Co^{2+} was observed in the larger cavities of MOR than those of ZSM-5. However, according to the literature (25, 28, 29), the sequence of Co^{2+} siting tendency in MOR differs from that in ZSM-5: the primary site is an α site, followed by a β site. In contrast, Descorme *et al.* suggested that the isolated Pd^{2+} in MOR is supposed to be located in a side pocket of MOR corresponding to β sites, and a gradual change in siting is observed in the sites facing the main, straight channel of MOR, that is, the α sites, resulting in a gradual increase in NO conversion (32). We conclude that some correlation exists between the ion-exchange property of the isolated Pd^{2+} in HMOR and the gradual change and subsequent stability of the Pd/HMOR in NO conversion. The ion-exchange of the isolated Pd^{2+} in the Pd/HMOR, evaluated by NaCl titration, was found to take a longer time to elute all of the isolated Pd^{2+} cations, indicating that the isolated Pd^{2+} is primarily stabilized in the less active β site in side pockets of MOR. Further, the higher NO conversion of Pd–Co(3)/HMOR from the beginning of a reaction without an increase in the activity suggests that the isolated Pd^{2+} in



$$Z^-Pd^{2+}Z^- + 2H_2O \rightarrow Pd^{2+}(OH^-)_2 + 2H^+Z^-$$

FIG. 8. Illustration of isolated Pd^{2+} and Co^{2+} sitings in ZSM-5 cavities.

the catalyst might exist in the more active α sites, and it may interact with the α-siting Co^{2+} in the same straight channel of MOR.

In summary, the characteristic properties of isolated Pd^{2+} cations are clarified by locating them in the ion-exchange sites of zeolites. Also, the promising effect of isolated Co^{2+} cations on stabilizing the mobile, isolated Pd^{2+} is developed by intimate siting in the zeolite cavities, as has been proposed using Ir/In-zeolites (33). Therefore, for the high performance of metal cations, zeolite must act as a ligand (34) by which cationic species are stabilized, or as a solid solvent in which the cationic species act freely, resulting in pronounced catalytic activity and selectivity, which would never be attained as metal, metal oxide, or on oxide supports.

CONCLUSIONS

Palladium ion-exchanged zeolite catalysts were tested to evaluate their catalytic properties toward CH_4-SCR in the presence of water vapor at a relatively high temperature of 500°C. Pd/HZSM-5 with a Si/Al ratio of 19.8 deactivated under the reaction conditions. When the Si/Al ratio decreased, the durability was slightly enhanced but the NO conversion gradually decreased. Among the zeolites tested, mordenite-supported palladium showed stability in NO conversion during the durability test reaction.

The addition of cobalt on Pd/HZSM-5 improved the catalytic stability, and no deactivation was observed on the sample loaded 3.3 wt% cobalt. An isolated Pd^{2+} on HZSM-5, which was the active and selective site for CH_4-SCR, was not eluted by means of NaCl titration after the addition of 3.3 wt% cobalt. In contrast, NH_4NO_3 titration revealed that the isolated Pd^{2+} existed on the Pd–Co(3)/HZSM-5. We also found by the titration that some portion of cobalt was located as an isolated Co^{2+} in the sample. XPS results suggested that the isolated Co^{2+} cations change an electronic density within a local range of zeolite cavities, and then change the ion-exchange property of the isolated Pd^{2+}. The thermodynamic affinity of the isolated Pd^{2+} to ZSM-5 was enhanced by the addition of the isolated Co^{2+}, leading to a higher stability than Pd/HZSM-5 under the durability conditions. The effect of the isolated Co^{2+} on the stability of the isolated Pd^{2+} was observed not only on ZSM-5 with a different Si/Al ratio but also on zeolites having different size cavities, such as MOR. The isolated Pd^{2+} and Co^{2+} should be sited intimately in zeolite cavities to interact with each other. An isolated metal cation such as Pd^{2+} is stabilized by a ligature with a ligand-like complex such as Co^{2+} zeolites.

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