

# Mechanistic study of SCR-NO with methane over Pd-loaded BEA zeolite

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## Abstract

The SCR of NO with methane in excess oxygen was carried out over Pd-exchanged BEA zeolites prepared by two different methods; one is exchanged with Pd on H-BEA zeolites (Si/Al = 12.5) having organic template in zeolite and the other on H-BEA without template. The Pd-exchange on BEA in the presence of organic compound is an efficient way to introduce PdO species selectively onto the external site of zeolite pore, which seemed to be responsible for the enhanced SCR activity at lower temperature. This synergistic effect could be explained by the bifunctional role of PdO clusters for an easier activation of methane and ion exchanged Pd<sup>2+</sup> or protonic site of zeolite for the reduction of NO with the activated methane. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* BEA zeolite; SCR; Methane

## 1. Introduction

Since methane is one of the most difficult hydrocarbons to be activated, high temperature and reactive catalytic systems are needed to be utilized as a reductant in the SCR of NO. Only limited catalysts such as Pd-, Pt-, Co-, Ga- and Ir-zeolites were suggested for the CH<sub>4</sub>-SCR in excess oxygen [1–5], but these catalysts are still limited in practical applications due to the sensitive dependence of activity on the water vapor. Among these catalysts, Pd-zeolites such as Pd/ZSM-5 are known to be resistive for the

water vapor and interested in the CH<sub>4</sub>-SCR [6–8].

Metal-exchanged zeolite catalysts have been proven to be active in the SCR of NO<sub>x</sub> by hydrocarbons, but the reactivity and selectivity depend strongly on the nature of exchanged metal species and the types of hydrocarbons [9,10]. With Cu/ZSM-5, the NO<sub>x</sub> species are reduced only by C<sub>3+</sub> paraffins or C<sub>2+</sub> olefins but not by methane [11]. On the other hand, over M/ZSM-5 with M = Co, Pd, Pt the NO<sub>x</sub> species could be reduced by methane and consequently the SCR of NO<sub>x</sub> is possible by methane as well as higher hydrocarbons [3,9,12].

Recently, it was found that when the zeolites are over-exchanged or extra metal oxides are loaded together with metal-exchanged zeolites, the reaction temperature was lowered and the

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reactivity was higher than that of pure metal-exchanged zeolites; PdO with Pd/ZSM-5 in CH<sub>4</sub>-SCR of NO and Co<sub>3</sub>O<sub>4</sub> with Co/ZSM-5 in C<sub>3</sub>H<sub>6</sub>-SCR of NO [7,13,14]. This synergistic effect in excess oxygen has been explained by the bifunctional role of metal oxide cluster and protonic or metal-exchanged sites of zeolite. So, the cluster size and location of Co<sub>3</sub>O<sub>4</sub> on Co/ZSM-5 were controlled to optimize catalyst for C<sub>3</sub>H<sub>6</sub>-SCR of NO in the presence of excess oxygen, and an affirmative result was obtained [13,14]. We expanded this idea to design the Pd/BEA zeolite efficient for CH<sub>4</sub>-SCR of NO in excess oxygen.

In this study, Pd/BEA catalyst was prepared by two different methods to control the size and location of Pd on zeolite; one is ion-exchanged on as-synthesized H-BEA (Si/Al = 12.5) containing organic template in zeolite pore (Pd/BEA(S)), and the other on calcined H-BEA without template (PdC/BEA). We tried to elucidate the role of Pd clusters and ionic species on the zeolite in the SCR of NO with methane by monitoring the surface species using in situ FT-IR. We also gave understandings of the particle size, particle distribution and the nature of active species using various analytic techniques such as transmission electron microscopy (TEM), temperature-programmed reduction (TPR), XRD, chemisorption, ESR and UV-Vis DRS. Their catalytic activity was compared and evaluated by performing SCR of NO with methane.

## 2. Experimental

Palladium containing BEA zeolites (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 25, PQ) were prepared from BEA(S) and BEA(C), where BEA(S) denotes as-synthesized BEA zeolite containing organic template and BEA(C) indicates calcined BEA(S) without template. Various Pd-containing BEA zeolites with different loadings were prepared by conventional ion-exchange method by adding a calculated amount of PdCl<sub>2</sub> and NH<sub>4</sub>OH. The

evaporation method was used to prepare 1 wt.% Pd/SiO<sub>2</sub>.

The SCR activity of the catalysts was measured using quartz micro reactor in the following conditions: 1500 ppm NO, 4500 ppm CH<sub>4</sub>, 3% O<sub>2</sub>, GHSV = 24,000 h<sup>-1</sup>. Surface species were monitored under transient or steady-state reaction conditions using in situ DRIFT FT-IR cell. The DRIFT spectra were obtained using Nicolet Magna 560 spectrometer equipped with liquid nitrogen cooled MCT detector in real SCR conditions while heating up the sample. UV-Vis DRS spectra were obtained on a Shimadzu spectrophotometer (UV 2501PC). TEM images of the prepared Pd/BEA(S) and Pd/BEA(C) samples were obtained on a JEOL transmission. Electron microscope (model 300EX) was operated at 500 kV. NH<sub>3</sub> TPD was carried out in a GC (HP5890) apparatus in order to determine the total acidity of the solids. The catalysts under study were saturated with ammonia, and fluxed with an inert gas (He) while the temperature was increased in a linear program (heating rate of 10°C/min). TPR experiments were carried out in a homemade equipment with a TCD detector by modifying commercial GC using 5% H<sub>2</sub>/N<sub>2</sub> mixture. The heating rate was 10°C/min and the catalyst's weight was 0.3 g. Before the measurements, the samples were calcined in air flow at 500°C for 2 h. ESR spectra were recorded at 77 K with a Bruker ESP 300. The magnetic field was calibrated with a Bruker ERO 35M gauss meter. The microwave frequency was measured at a Hewlett-Packard HP 5342A frequency counter.

## 3. Results and discussion

Fig. 1 shows the UV-Vis diffuse reflectance spectra of five different dehydrated Pd-containing samples. For the reduced 1 wt.% Pd/SiO<sub>2</sub>, there is a broad absorption band over the whole range. However, after calcination, absorption band below 500 nm decreases drastically indicating that some of the reduced Pd species has

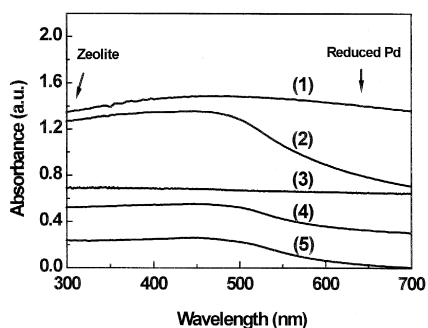


Fig. 1. UV-Vis DRS of Pd loaded samples. (1) Reduced 1 wt.% Pd/SiO<sub>2</sub>. (2) Calcined 1 wt.% Pd/SiO<sub>2</sub>. (3) Reduced 1 wt.% Pd/BEA(S). (4) Calcined 1 wt.% Pd/BEA(S). (5) After reaction of sample (4).

been oxidized into PdO. Meanwhile, every calcined sample and sample after reaction are quite similar to each other, giving a broad band around 500 nm, being brownish. It is known that the brown color is due to Pd<sup>2+</sup> [15]. The absorption band at around 200 nm is attributed to zeolite itself. From DRS result, it seems that, during the selective catalytic reduction of NO in the presence of excess oxygen atmosphere, some of Pd species might be oxidized and exists as PdO and Pd<sup>2+</sup> states.

In order to determine the Pd-metal particle dispersion H<sub>2</sub>-O<sub>2</sub> titration method was employed using a chemisorption apparatus (Micromeritics ASAP2010). Table 1 lists the metal dispersion and metallic surface area of the various Pd-containing BEA zeolite with different loadings. For Pd/BEA(S), as Pd loading increased from 0.5 to 3.0 wt.%, dispersion decreased linearly from 84% to 36% and metallic surface area increased. Interestingly, 1 wt.% Pd/BEA(C) shows poor metal dispersion and metallic surface area compare to that of 1 wt.% Pd/BEA(S) by a factor of 1.5. This result is in

Table 1

Metal dispersion and metallic surface area of Pd/BEA(S) and Pd/BEA(C) with different Pd contents

	Pd/BEA(S)			Pd/BEA(C)
Pd content (wt.%)	0.5	1	3	1
Metal dispersion (%)	83.9	54.1	35.7	34.8
Metallic surface area (m <sup>2</sup> /g)	1.88	2.41	4.81	1.55

a good agreement with the TEM result. While 1 wt.% Pd/BEA(S) shows about 28 Å Pd metal particle, 1 wt.% Pd/BEA(C) shows Pd metal particle of 60 Å. According to Benesi et al., high dispersions may be obtained if NH<sub>4</sub>OH is added to the aq. solution of PdCl<sub>2</sub> for making a complex of soluble [Pd(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> and also to maintain a pH of 9–10, which creates a negative surface charge and increases the adsorption capacity for [Pd(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> ion [16]. The higher dispersion of Pd metals in Pd/BEA(S) could be explained as follows. During the ion-exchange process, [Pd(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> ions cannot easily penetrate into as-synthesized BEA zeolite, BEA(S), whose pores are blocked by the template. Hence, most of [Pd(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> ions are deposited on the surface of BEA zeolite, and during the calcination, [Pd(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> and template decompose, PdO and/or Pd<sup>2+</sup> are developed and migrate into the pore of BEA zeolite, which induces higher dispersion of Pd metal. On the other hand, when calcined BEA zeolite is employed, [Pd(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> ions can be ion-exchanged not only on the surface but also inside the zeolite pores. Similarly during the calcination of this sample, formed PdO and/or Pd<sup>2+</sup> migrate, aggregate and produce bigger clusters. This PdO species was confirmed by XRD. PdO peaks at 33° and 44° were clearly observed for both 1 wt.% Pd/BEA(S) and 1 wt.% Pd/BEA(C).

The redox behavior of Pd species formed in BEA zeolite has been studied by TPR. Prior to the measurements, the samples were calcined in air flow at 500°C for 2 h. Fig. 2 demonstrates

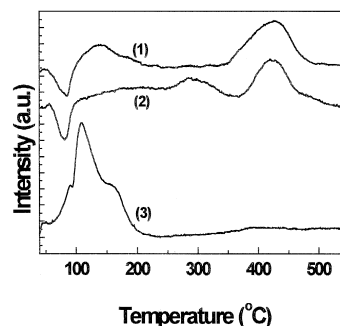


Fig. 2. TPR of Pd-loaded samples. (1) 1.0 wt.% Pd/BEA(S), (2) 1.0 wt.% Pd/BEA(C), (3) 1.0 wt.% Pd/SiO<sub>2</sub>.

three Pd-containing samples with different supports.

TPR of 1.0 wt.% Pd/SiO<sub>2</sub> shows a strong peak at 110°C and a shoulder at 160°C, which is attributed to the reduction of Pd-oxide species [17]. Since 1 wt.% Pd/BEA(S) catalyst shows the highest SCR activity, the redox ability of it is compared with 1 wt.% Pd/BEA(C). TPR results reveal the appearance of mainly two peaks for 1 wt.% Pd/BEA(S) at 140°C and 420°C. These peaks are assigned to the reduction of PdO located on the outer surface and ion-exchanged Pd<sup>2+</sup>, respectively. For 1 wt.% Pd/BEA(C), on the other hand, two main peaks at 290°C and 420°C are observed. The peak at 290°C is assigned to the reduction of PdO located inside the zeolite pore. The reduction temperature of PdO depends on its location, inner or outer surface of zeolite BEA pore.

In order to determine chemical state of palladium in Pd/BEA(S) and Pd/BEA(C), ESR was attempted. No ESR signals were seen in the calcined samples. Heating under vacuum at 550°C for 3 h generated a singlet centered at  $g = 2.0023$ , which can be assigned to thermally reduced Pd<sup>0</sup>. The singlet intensity for reduced Pd/BEA(S) is 1.5 times higher than that for reduced Pd/BEA(C). Heating under evacuation at 400°C with the calcined sample, for both samples, typical Pd<sup>+</sup> ESR signal was detected, which consists of  $g_{\parallel} = 2.383$  and 2.316, and  $g_{\perp} = 2.158$ . And also this Pd<sup>+</sup> peak intensity for reduced Pd/BEA(S) is about two times greater than for reduced Pd/BEA(C). From the ESR study, it seems that there are at least two different Pd ion locations in the zeolite BEA and Pd in Pd/BEA(S) is easier for reduction than in Pd/BEA(C), which is a supporting evidence for TPR.

Conclusively, dispersion, size, and chemical state of Pd species in a zeolite catalyst are important factors for controlling the catalytic reduction of NO by methane in the presence of excess oxygen. Attempt for the preparation of effective catalyst with BEA(S) is successful. Synergistically, both highly dispersed PdO and

Pd<sup>2+</sup> are catalytically active for the abatement of NO by methane.

### 3.1. SCR activity

Pd was loaded on four different types of supports, and the SCR of NO with methane was carried out in excess oxygen (Fig. 3). Among the four catalysts, Pd/BEA(S) prepared by ion-exchange with uncalcined H-BEA containing template in zeolite pore showed the highest SCR activity. The activity enhancement was 30% higher than that of Pd/BEA(C) prepared by ion-exchange with calcined H-BEA. The reaction temperature also shifted from 600°C to 450°C in the case of Pd/BEA(S). The SCR activity at 600°C was observed only for

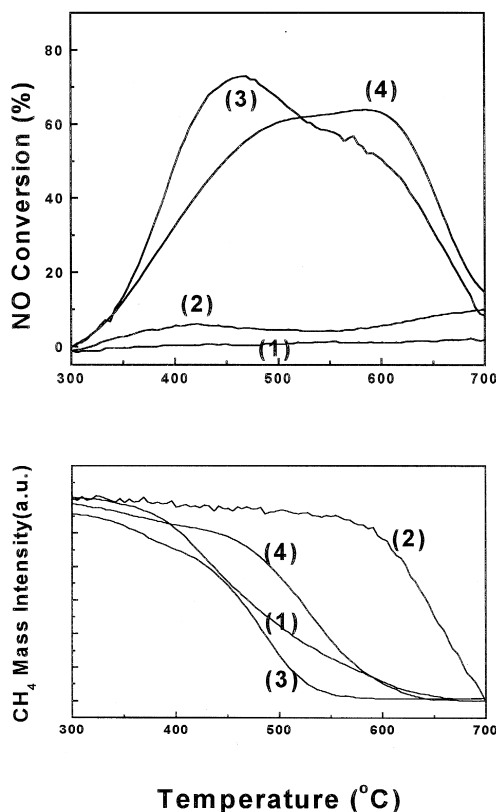


Fig. 3. SCR activity of Pd-exchanged BEA catalyst: (1) 1 wt.% Pd/SiO<sub>2</sub>, (2) H-BEA, (3) 1 wt.% Pd/BEA(S) and (4) 1 wt.% Pd/BEA(C); (1500 ppm NO + 3% O<sub>2</sub> + 4500 ppm CH<sub>4</sub>, GHSV = 24,000 h<sup>-1</sup>).

Pd/BEA with low loading of Pd and could be ascribed to the purely ion-exchanged Pd<sup>2+</sup> on H-BEA zeolite. As Pd loading increases, the SCR activity enhances and simultaneously reaction temperature is lowered to 450°C. According to our previous results [13,14], this enhanced catalytic performance is closely related with the light off temperature of methane and the Pd/BEA(S) having high methane combustion activity at lower temperature shows the highest SCR activity. However, one more thing to be considered is that methane combustion activity is not enough for the selective reduction of NO in excess oxygen atmosphere. Pd supported on silica (Pd/SiO<sub>2</sub>) also shows almost the same combustion activity as that of Pd/BEA(S), but it does not show any SCR activity. According to Burch and Ramli [18], Pd/SiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> without protonic and Pd<sup>2+</sup> ionic sites are active for the reduction of NO by methane in oxygen free but their activities decrease rapidly as the oxygen concentration increases and most of the methane is combusted. This means that Pd<sup>2+</sup> ions exchanged in zeolite are inevitably necessary for the selective reduction of NO by methane in excess oxygen atmosphere. The importance of zeolite in selective reduction of NO with methane was also insisted by Ogura et al. [19]. Under the SCR conditions, the concentration of oxygen is 20 times higher than that of NO and methane to be used as a reductant instead of combustion must selectively interact with NO [20]. So, for selective reduction of NO<sub>x</sub> with diluted methane, probably it is a surface reaction between adsorbed NO<sub>x</sub> and activated methane species instead of gas phase reactions. Compared to the PdO clusters on Pd/SiO<sub>2</sub>, Pd<sup>2+</sup> ions exchanged on zeolite provide strong adsorption site for NO<sub>x</sub> in excess oxygen, so it will increase the possibilities of selective interaction between NO<sub>x</sub> and activated methane. The enhanced NO<sub>x</sub> adsorption on Pd/BEA could be seen clearly in IR spectra (Fig. 4).

However, Pd<sup>2+</sup> or protonic sites are not effective for methane activation and show poor

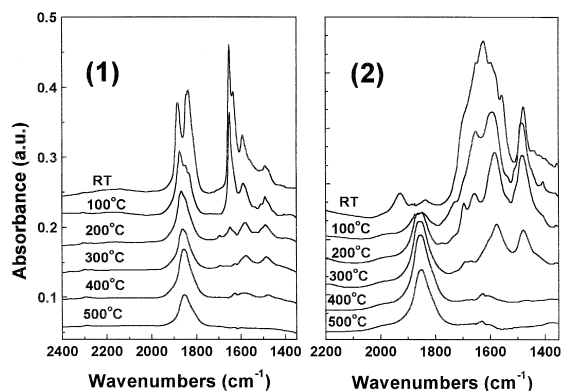


Fig. 4. In situ FT-IR spectra of (1) Pd/BEA(C) and (2) Pd/BEA(S) in 1500 ppm NO + 3% O<sub>2</sub>, GHSV = 24,000 h<sup>-1</sup>.

combustion activity (Fig. 3(2) and 3(4)). The light-off temperature of 0.3 wt.% Pd/BEA(S) is higher than 500°C, so it was impossible to obtain SCR activity below 500°C. Pure H-BEA also did not show any combustion activity below 500°C and it has no SCR activity.

According to the recent results of Kumthekar and Ozkan et al. [21–23], PdO clusters are one of the most effective catalysts for the combustion of CH<sub>4</sub> and in excess oxygen Pd exists as PdO. The UV-Vis DRS results also show that considerable amount of Pd on BEA after calcination exists as PdO and its state is maintained in SCR reaction (Fig. 1).

To elucidate more clearly the role of PdO clusters dispersed near zeolite pore, Pd/BEA catalysts were prepared while controlling the size and location of loaded Pd on zeolite by introducing organic templates in zeolite pores before Pd exchange. For Pd/BEA(S) prepared in the presence of organic template, PdO clusters could be located preferably outside of zeolite pores with high dispersion and the SCR activity was enhanced. So, this synergistic effect on Pd/BEA(S) could be explained by the co-presence of PdO clusters near the zeolite pores together with protonic or Pd<sup>2+</sup> ions. Though the results are not shown, at low loading of Pd, the SCR activity was observed only at around 600°C and as the exchange level of Pd increases the reaction temperature shifts to 500°C. The reason

for SCR activity at low temperature could be ascribed by the presence of extra Pd clusters located near the Pd-exchanged BEA catalyst. The similar results were observed in the SCR of NO with propylene over  $\text{Co}_3\text{O}_4$ -loaded ZSM-5 where reaction temperature lowered by 200°C and 75% activity enhancement in SCR activity due to the co-presence of  $\text{Co}_3\text{O}_4$  effective propylene activation [14].

The importance of acid site in the SCR of NO with hydrocarbons was emphasized by Misono et al. and Adelman and Sachtler [7,17]. According to the  $\text{NH}_3$  TPD, Pd/BEA also maintains considerable amount of acid sites at 400–500°C even after Pd exchange. However, Pd/ $\text{SiO}_2$  does not have any acidity. This shows that protonic sites are related with SCR activity but still it is not clear in which step they are involved. One postulation is that though protonic site itself is not active for methane activation it could stabilize activated hydrocarbon species for further interaction with adsorbed  $\text{NO}_x$  species on  $\text{Pd}^{2+}$  ionic sites.

### 3.2. Surface species

To understand the difference in SCR activity of Pd/BEA(S) and Pd/BEA(C), surface species were monitored under  $\text{NO} + \text{O}_2$ ,  $\text{NO} + \text{CH}_4$ ,  $\text{CH}_4 + \text{O}_2$  and SCR conditions using in situ FT-IR; GHSV = 24,000  $\text{h}^{-1}$ , 1500 ppm NO + 4500 ppm  $\text{CH}_4$  + 3%  $\text{O}_2$ . As shown in Fig. 5, under  $\text{NO} + \text{O}_2$  conditions, various highly oxidized  $\text{NO}_x$  species (1400–1700  $\text{cm}^{-1}$ ) such as  $\text{N}_2\text{O}_4$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_3$ , and  $\text{NO}_3$  were preferentially formed on Pd/BEA(S) while only nitrosyl species (1800–1950  $\text{cm}^{-1}$ ) on Pd/BEA(C). These formed nitrite and nitrate species are stable at room temperature. These oxidized  $\text{NO}_x$  species are not stable above 300°C on Pd/BEA(C) but on Pd/BEA(S). These oxidized  $\text{NO}_x$  species are supposed to be formed on isolated  $\text{Pd}^{2+}$ s, which are ion exchanged into H-BEA. All of these  $\text{NO}_x$  species converted to nitrosyl species above 400°C on both catalysts.

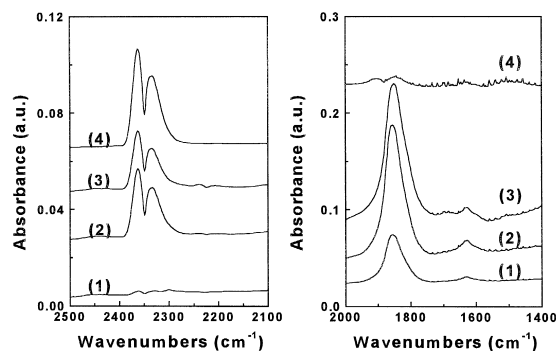


Fig. 5. In situ FT-IR spectra of (1) H-BEA, (2) 1 wt.% Pd/BEA(C), (3) 1 wt.% Pd/BEA(S) and (4) 1 wt.% Pd/ $\text{SiO}_2$  in SCR condition; 1500 ppm NO + 4500 ppm  $\text{CH}_4$  + 3%  $\text{O}_2$  and GHSV = 24,000  $\text{h}^{-1}$ .

Surface species adsorbed on various samples under SCR conditions at 400°C are displayed in Fig. 5. All of the Pd-loaded BEA catalysts showed high intensity of  $\text{CO}_2$  absorption bands at 2300 and 2700  $\text{cm}^{-1}$ , which implies that higher Pd has high oxidation ability of  $\text{CH}_4$  into  $\text{CO}_2$ . However, different from Pd-loaded BEA, BEA showed poor oxidation ability and  $\text{CO}_2$  peak is very low. In  $\text{NO}_x$  adsorption, these catalyst also showed quite a different behavior. On Pd/ $\text{SiO}_2$  with no isolated  $\text{Pd}^{2+}$  sites, no surface  $\text{NO}_x$  species were observed, but on all the other catalysts containing BEA strong nitrosyl species were observed even above 400°C. It seems that ion-exchanged  $\text{Pd}^{2+}$  serves as a stronger adsorption of NO than H-BEA itself. Therefore, the enhanced SCR activity on PdS/BEA could be explained by the increased surface  $\text{NO}_x$  species and promoted methane by the Pd cluster dispersed on the external site of H-BEA zeolite.

## 4. Conclusions

Based on catalytic performance over Pd-loaded catalysts in the SCR of NO with  $\text{CH}_4$  and analytical investigation of the catalyst prepared in this work, the following conclusions may be drawn.

Dispersion, size, and chemical state of Pd species in a zeolite catalyst are important factors

for controlling the catalytic reduction of NO by methane in the presence of excess oxygen. Attempt for the loading of palladium using BEA(S) with conventional ion-exchange method is successful, while BEA(C) is not. The optimum catalytic activity is obtained at 1.0 wt.%. Both highly dispersed PdO, Pd<sup>2+</sup> and protonic sites are catalytically active for the abatement of NO by methane, and protonic sites are catalytically active for the abatement of NO by methane and showed synergistic activity when they were combined properly. Under SCR conditions, multifunctional role of Pd/BEA can be put forward: (1) PdO clusters prevail on Pd/BEA(S) and favorable for redox cycle, (2) PdO clusters located on external surface of the zeolite pore are effective for the CH<sub>4</sub> activation particularly at lower reaction temperature, (3) isolated Pd<sup>2+</sup> or protonic site may serve as centers of the reduction of NO, and (4) enhanced NO<sub>x</sub> formation and adsorption on Pd/BEA(S) can be attributed to the improved SCR activity.

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