Selective Catalytic Reduction of NO by Methane over Pd Loaded on Heteropolyacids/SiO_2 at Low Temperature

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Pd was loaded on heteropolyacids/SiO_2, and used for the selective reduction of NO with methane in the presence of oxygen and moisture. The catalyst exhibited activity in the selective reduction of NO in the temperature range between 473 and 573 K. The temperature was significantly lower than that in the conventional catalysts, such as Pd-loaded zeolites or monolayer-type oxides. Among tested heteropolyacids, $H_3PW_{12}O_{40}$ gave rise to the highest activity in the reaction. The catalytic performance was improved by the addition of water vapor. The generation of highly dispersed PdO species was observed in the Pd K-edge EXAFS spectra, whose structure was similar to those found in the conventional Pd-loaded zeolites catalyst. The reason for the evolution of NO reduction activity over Pd/$H_3PW_{12}O_{40}$/SiO_2 was attributed to the formation of NOH^+, as measured by IR, in addition to the generation of highly dispersed PdO species at low temperature on the Brønsted acid sites of heteropolyacid.

Recently, much effort has been devoted to the removal of NO_x, which can cause acid rain and air pollution. The catalytic abatement of NO_x using hydrocarbons as reducing agents is one of the promising ways to solve the problem. In previous investigations, various kinds of supported metal catalysts, including Co, Ga, Mn, Pd, and Ag, were found to catalyze the reduction of NO with methane.[1–5] However, sometimes the activity was irreversibly reduced under moisture. Among these noble metals, Pd has been widely investigated as a promising candidate for the removal of NO using methane because of its high activity and tolerance to water vapor.[1] It has been known that the use of supports with the Brønsted acid character was indispensable to exhibit activity in Pd catalysts. Therefore, HZSM-5 or HMordenite having Brønsted acidity has been employed as a support for Pd.[6] However, the Brønsted acidity of zeolites was readily lost through dealumination under moisture present in the practical reaction conditions. In order to overcome the drawback of zeolites, acidic oxides, such as SO_4^{2-}/ZrO_2 and WO_3/ZrO_2, were tried to be used as alternative supports for Pd.[7–9] These monolayer-type oxides were advantageous in that they possessed strong Brønsted acidity and a mechanistic stability. In the present study, heteropoly acids (HPs) having strong Brønsted acidity were employed for the support of Pd as an extension of various studies of Pd deNO_x catalysts. A novel catalytic performance is expected to evolve when HP is used as a support for Pd due to their strong Brønsted acidity, comparable to that of acid from zeolites, in addition to the NO adsorption capacity of HPs through the displacement of water present in the secondary structure (pseudo-liquid phase) of Keggin anions.[10–15] Using this unique property of HPs, an attempt was made to decompose the adsorbed NO into N_2 by rapid heating. Particularly, extensive studies were carried out using trihydrogen phosphododecatungstate ($H_3PW_{12}O_{40}$, HPW) as a sorbent for NO. In addition to the direct decomposition of adsorbed NO, ammonium cation was examined as a source of ammonia to reduce NO to N_2.[14,15] Although these studies aimed at stoichiometric reactions using HPs sorbent, HPs have not been used as catalyst for selective reduction of NO so far. In this study, three kinds of HPs, namely $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, and $H_4SiW_{12}O_{40}$, were used as supports for Pd. In order to expand the surface areas of HPs, they were dispersed over a SiO_2 surface as a monolayer-type oxide prior to the loading of Pd. Among the tested HPs, HPW was studied most intensively because it exhibited a superior catalytic performance over that of other HPs. The influence of the composition of these catalysts and the effect of water vapor was also examined. The catalytic performance was correlated with the local structure and adsorbed NO species, as measured by means of EXAFS and the IR method. The overall objective of this study was the removal of NO and hydrocarbons emitted during the cold-start period in vehicles simultaneously,while making use of the ability of HPs in the adsorption of NO_x as well as polar molecules.[16] Here, methane was employed as a reductant among hydrocarbons at the beginning of the investigation, which seemed to be most difficult to be used for the selective reduction of NO.

Experimental

Sample Preparation. $H_3PW_{12}O_{40}\cdot nH_2O$, $H_3PMo_{12}O_{40}\cdot nH_2O$, and $H_4SiW_{12}O_{40}\cdot 26H_2O$ (Wako Chemicals) were dissolved in methanol, and they were impregnated on SiO_2 (N602A, Nikki Chemical). The loading of HPs was varied from 20 to 40 wt %. Pd was impregnated on these HPs/SiO_2 using a toluene solution of palladium(II) acetate (Wako Chemicals). Toluene was used to keep the HP on a SiO_2 surface during the impregnation of Pd.[17] In order to compare with the catalytic performance of a zeolite support, Pd was also loaded onto HZSM-5. HZSM-5 was prepared by an ion exchange of ZSM-5 (Tosoh Co., Si/Al_2 = 23.8) with a NH_4NO_3 solution at 353 K for 24 h, followed by calcination under N_2 at 773 K for 4 h. Pd (0.2 wt %) was introduced to HZSM-5 with an ion-exchange method a using 0.01 $mol\,dm^{-3}$ $[Pd(NH_3)_4]Cl_2$ (Aldrich) solution at 353 K for

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24 h. The catalysts were subsequently filtered, washed, and dried at 373 K, followed by calcination in a N_2 flow (30 mL min^{-1}) at 773 K for 4 h.

Catalytic Reaction. A catalytic reaction was carried out using a fixed-bed flow reactor. The catalysts were sieved to 50–80 mesh. No pretreatments were undertaken to prevent the destruction of HP at high temperature. A mixture of NO, O_2, methane, and water vapor (NO, 1000 ppm; CH_4, 1000 ppm; O_2, 1%; water vapor, 10%; He balance; total flow rate, 150 mL min^{-1}) was fed into 2 g of the catalyst. The outlet gas was analyzed by a gas chromatograph (Hitachi 163) equipped with a TCD detector and a chemiluminescence NO_x meter (Horiba). The effluent gas was analyzed with Molecular sieve 13X and Porapak Q columns. Water was fed into the reactor using a microfeeder, which was vaporized at the inlet of the reactor, and then mixed with the reactant gas mixture.

XAFS Measurements and Analysis. W L_3-edge (10.2 keV) and Pd K-edge (24.3 keV) XAFS data were collected at the BL10B station of the Photon Factory of the High Energy Accelerator Research Organization (KEK). The storage ring was operated at 2.5 GeV with a ring current of 300–450 mA. A channel-cut Si(311) single crystal was used to obtain a monochromatic X-ray beam. The incident beam was detuned by 40% in order to eliminate the higher harmonics. The measurement was carried out in a transmission mode at room temperature. For the measurement of W L_3-edge, ion chambers filled with N_2 and N_2 (50%)/Ar (50%) were used for I_0 and I, respectively. To measure the Pd K-edge spectra, ion chambers were filled with Ar and Kr for detectors of I_0 and I, respectively. The energy was calibrated using a W foil and Pd a foil for W L_3-edge and Pd K-edge, respectively. To prepare reacted samples, the catalytic reaction was carried out for 4 h, and then the flowing gas was switched to He and the reactor cell was cooled down to room temperature. The samples were pressed into a wafer form in air. The data were analyzed using the REX2000 Ver.2.0.4 program (Rigaku). Fourier transforms of $k^3\chi(k)$ data were performed in the k range of 20–160 and 30–118 nm^{-1} for the analysis of W L_3-edge and Pd K-edge spectra, respectively.

IR Measurement. IR spectra were measured using a Perkin Elmer Spectrum One spectrometer. A wafer form of sample was placed in a quartz in-situ cell. The sample was treated with the reaction gas mixture (NO, 1000 ppm; CH_4, 1000 ppm; O_2, 1%; He balance; total flow rate, 150 mL min^{-1}) at 473 K for 4 h, followed by a replacement with He flow. The IR spectra were measured before the reaction and after cooling down to room temperature.

Results and Discussion

Catalytic Performance of Pd/Heteropolyacid/SiO$_2$. Initially, the dependence of the temperature on the catalytic activity of Pd was studied over a Pd/HPW/SiO$_2$ catalyst. The conversion of NO and methane over Pd/HPW/SiO$_2$ (Pd loading: 1 wt %, HPW loading: 30 wt %) is given in Fig. 1. The measurement was carried out after 3–4 h from the beginning of the reaction at given temperatures when the catalysis reached stationary performance. The reaction commenced at 473 K, and the highest conversion of NO (12%) was reached at 573 K. Interestingly, the temperature almost agreed with the optimum condition observed in HPW for the adsorption of NO. Namely, the temperature range for adsorption of NO over HPW was reported to be 423–473 K.[18] It should be notified that the temperature was considerably lower than that for conventional Pd/zeolite or monolayer type catalysts. That is to say, on Pd over HZSM-5, HMordenite or monolayer-type supports (SO_4^{2-}/ZrO_2, WO_3/ZrO_2), the onset temperature was found at around 623 K, and the maximum conversion of NO was attained at 723–773 K.[19,20] On further raising the temperature, the activity of Pd/HPW/SiO$_2$ decreased, whereas the conversion of methane to CO_2 continuously increased up to 823 K. Probably, the decline in the activity was caused by a reduction of the adsorption capacity of NO in HPW, in addition to the decomposition of the HPW structure at high temperature, as mentioned later. From a measurement of evolved N_2 using a TCD detector, it was confirmed that NO was selectively reduced with methane to form N_2. The selectivity of methane utilized for the reduction of NO was calculated to be 25% at 523 K. In order to determine the optimal composition of the catalyst, the reaction was carried out over catalysts with varied Pd loading (Fig. 2). Without the addition of Pd, namely 30 wt % HPW/SiO$_2$, the catalyst was totally inactive in the reaction. Thus, it was confirmed that the presence of Pd was indispensable in the reduction of NO. Accompanied by raising in the loading of Pd, the NO conversion continued to increase, while the conversion of methane passed the maximum value at 1.0% of Pd loading. Then, the reaction was performed by changing the loading of HPW. Figure 3 gives the dependence of NO and methane conversion on the amount of HPW, while the loading of Pd was fixed at 1.0 wt %. The maximum conversion of NO and methane was reached when 30 wt % of HPW was loaded on SiO$_2$. In the case of Pd loaded on HPW without the addition of SiO$_2$ or Pd loaded on SiO$_2$, the catalysts were considerably inactive in the reaction. Probably, the surface area of HPW itself was too small to generate dispersed PdO species, which was considered to be the active species in the reaction, as will be described later. From these data, it was confirmed that the combination of a SiO$_2$ support, HPW and Pd was required to exhibit the activity for Pd in the selective reduction of NO.

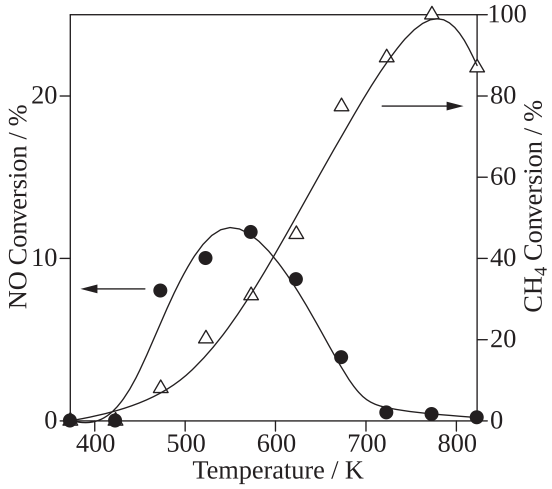

Fig. 1. Dependence of NO (●) and methane (△) conversion on the temperature over Pd/HPW/SiO$_2$; Pd loading: 1.0 wt %, HPW loading: 30 wt %; NO 1000 ppm, CH_4 1000 ppm, O_2 1%, water vapor 10%, total flow rate 150 mL min^{-1}.

In order to examine the kind of heteropolyacid, three types of HPs were dispersed over SiO$_2$, and then employed as sup-

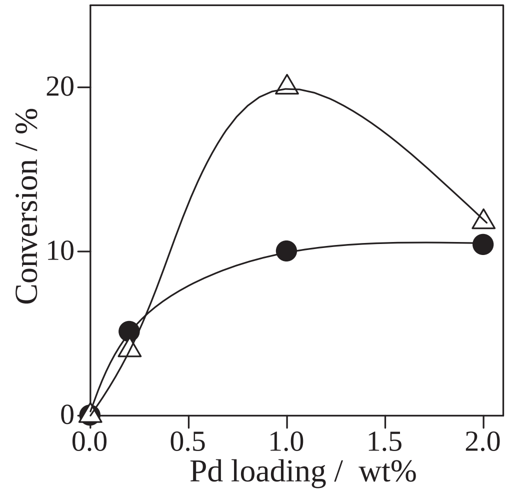

Fig. 2. Dependence of NO (●) and methane (△) conversion on the loading of Pd over Pd/HPW/SiO_2 catalyst; HPW loading: 30 wt %; NO 1000 ppm, CH_4 1000 ppm, O_2 1%, water vapor 10%, total flow rate 150 mL min^{-1}.

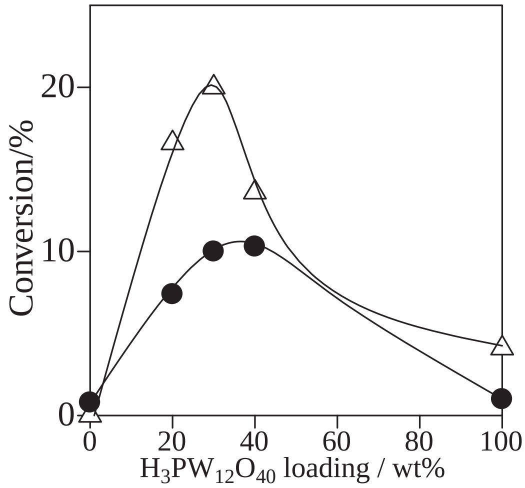

Fig. 3. Dependence of NO (●) and methane (△) conversion on the loading of HPW over Pd/HPW/SiO_2 catalyst; Pd loading: 1 wt %; NO 1000 ppm, CH_4 1000 ppm, O_2 1%, water vapor 10%, total flow rate 150 mL min^{-1}.

ports for Pd. Data concerning the conversions of NO and methane measured at 523 K are given in Fig. 4. The measurement was carried out after the reaction reached a stationary performance. The NO conversion decreased depending on the kinds of heteropolyacids in the following order: $H_3PW_{12}O_{40}$ > $H_3PMo_{12}O_{40}$ > $H_4SiW_{12}O_{40}$. The tendency was in good agreement with the order of the acid strength measured in aqueous solutions.[21] Probably, this agreement meant that the Brønsted acid strength of HPW is related to the adsorption strength or capacity of NO. Among these heteropolyacids, the highest conversion of NO was observed when $H_3PW_{12}O_{40}$ (HPW) was used as a support. In addition, the methane consumed in the reduction of NO was lowest over the Pd/HPW/SiO_2 catalyst. In other words, the selectivity of methane over Pd/HPW/SiO_2 was highest among tested heteropolyacids.

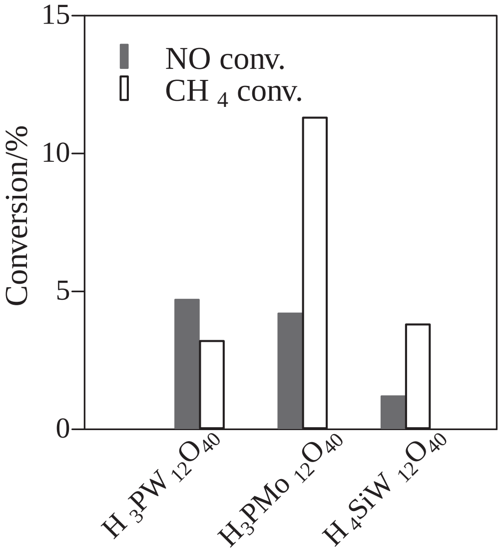

Fig. 4. NO and methane conversion over Pd/heteropoly acids/SiO_2 catalysts; Pd loading 0.2 wt %, heteropoly acids 20 wt %, NO 1000 ppm, CH_4 1000 ppm, O_2 1%, water vapor 10%, total flow rate 150 mL min^{-1}.

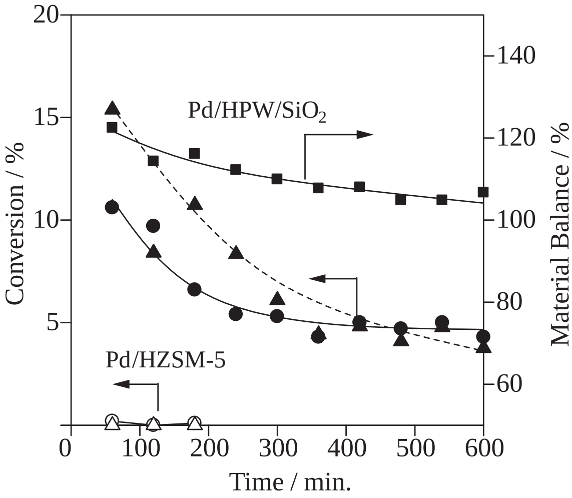

Fig. 5. Time-course change in the conversion of NO and methane over 0.2 wt % Pd/20 wt % HPW/SiO_2 (closed) and 0.2 wt % Pd/HZSM-5 (open) catalysts. (■) material balance of carbon on Pd/HPW/SiO_2, (●, ○) NO conversion, (▲, △) methane conversion. Temperature, 523 K; NO 1000 ppm, CH_4 1000 ppm, O_2 1%, water vapor 10%, total flow rate 150 mL min^{-1}.

Figure 5 shows the time-course change in the catalytic performance of Pd/HPW/SiO_2. The loadings of Pd and HPW were 0.2 and 20 wt %, respectively. The reaction was carried out at 523 K. In the beginning of the reaction, a relatively high conversion of NO was observed. The NO conversion gradually decreased and came to a stationary value at 5% after 350 min. Probably, the initial high activity was caused by the organic residue used in preparing the catalyst. The fact was evidenced from the material balance of carbon calculated based on the methane and the generated CO_2. Namely, the value exceeded

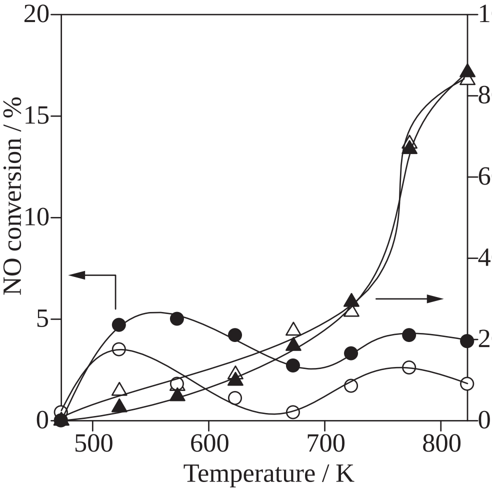

Fig. 6. Dependence of NO (●, ○) and methane (▲, △) conversion over Pd/HPW/SiO$_2$ on the temperature; Pd loading 0.2 wt %, heteropoly acids 20 wt %, NO 1000 ppm, CH$_4$ 1000 ppm, O$_2$ 1%, water vapor 10% (closed) or 0% (open), total flow rate 150 mL min^{-1}.

100% during 350 min from the beginning of the reaction, as given in the figure. The catalyst then exhibited steady performance. In agreement with the observation, NO reduction activity was significantly enhanced by using toluene as a reductant for NO at 573 K.[22] This fact suggested that a high NO reduction activity could be achieved when aromatics were used as reductants for NO in place of methane. A comparable reaction was undertaken over Pd (0.2 wt %)/HZSM-5 under the same conditions and catalyst weight. The Pd/HZSM-5 was totally inactive in the reaction under the reaction condition, as depicted in Fig. 5.

In order to examine the influence of water vapor on the catalytic performance of Pd, the reaction was carried out in an atmosphere of 10% water vapor or a dry condition, and the performance was compared (Fig. 6). As shown in the figure, the conversion of NO and methane measured under the dry condition was slightly lower than those carried out in the presence of 10% water vapor. Therefore, it can be noted that water vapor improved the catalytic activity of Pd/HPW/SiO$_2$. Although it was known that the strength of the Brønsted acidity of HPW was weakened by the addition of water vapor,[23] the adsorption of NO on HPW was enhanced in the co-presence of water vapor and O$_2$.[18] The addition of H$_2$O was necessary for NO substitution because the H$_2$O linkages connecting the Keggin structure were slowly removed in a dry atmosphere at the reaction temperature.[18] Therefore, the reason for the improvement in the activity may be ascribed to the promoting adsorption of NO into HPW. The appearance of the peaks in the NO conversion plot at 773 K (●, ○) may be resulted from the generation of the monolayer type WO$_3$/SiO$_2$ support possessing an acid character, which was generated by the decomposition of HPW over a SiO$_2$ support at high temperature.

Structural Characterization of Pd/HPW/SiO$_2$. Figure 7 gives the XRD patterns of HPW/SiO$_2$ with a varied loading of HPW. Diffraction peaks attributed to the crystal structure of HPW were observed in the samples with HPW loading above 40 wt %. However, no diffraction peaks appeared in the HPW/SiO$_2$ with HPW loading of less than 30 wt %. In a catalytic reaction over Pd/HPW/SiO$_2$ with different loadings of HPW, the highest activity was attained when 30–40 wt % of HPW was loaded on SiO$_2$, as shown in Fig. 3. Upon further increasing the loading of Pd, the NO reduction activity declined. Probably, this was due to a reduction in the surface area of HPW, which kept the dispersed form of PdO. Therefore, it was suggested that HPW was well dispersed over SiO$_2$ at the optimum loading for the reaction.

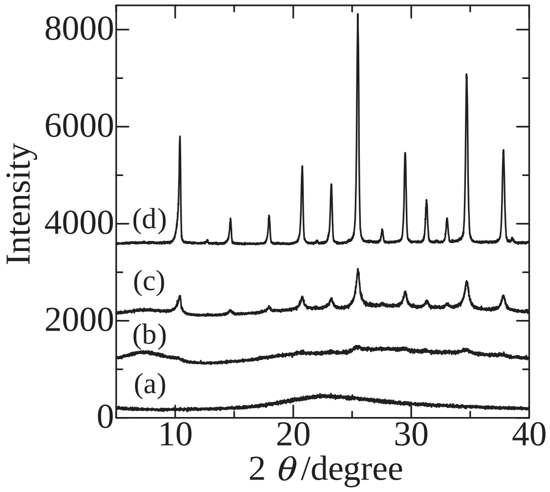

Fig. 7. XRD patterns of Pd loaded on H$_3$PW$_{12}$O$_{40}$/SiO$_2$; H$_3$PW$_{12}$O$_{40}$ loading: (a) 0 wt %, (b) 30 wt %, (c) 40 wt %, (d) 100 wt %.

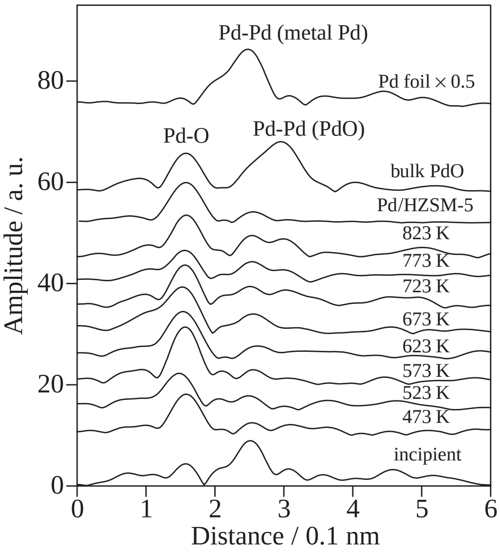

Fig. 8. Pd K-edge EXAFS Fourier transforms of Pd/HPW/SiO$_2$ catalysts measured before and after the catalytic reaction for 3 h at different temperatures and Pd/HZSM-5 (Si/Al$_2$ = 23.8) treated in O$_2$ at 773 K. Pd loading, 0.2 wt %; HPW loading, 20 wt %.

The local structure of Pd was measured by means of Pd K-edge EXAFS. Figure 8 shows Fourier transforms of the Pd K-edge EXAFS spectra of Pd/HPW/SiO$_2$ measured before and after the NO–CH$_4$–O$_2$–(H$_2$O) reaction at different temperatures. The loadings of Pd and HPW were 0.2 and 20 wt %, respectively. For the preparation of reacted samples, the Pd/HPW/SiO$_2$ was subjected to a reaction under 10% water vapor for 3 h. In the spectrum measured before the reaction, a peak appeared at 0.25 nm, which could be attributed to the nearest-neighboring bond of Pd–Pd in metal Pd from a comparison with that of a Pd foil. Probably, the impregnated Pd(OAc)$_2$ was reduced with an organic solvent to form metal Pd in preparing the preparation of catalyst. The peak of metal Pd–Pd disappeared after the reaction conducted at 473 K. Alternatively, a new peak appeared at 0.15 nm, which was assigned to the Pd–O bond of PdO, as can be seen from a comparison with the spectrum of bulk PdO. However, Pd–(O)–Pd characteristic of agglomerated PdO was not observed. This fact meant the generation of highly dispersed PdO over HPW/SiO$_2$ after the reaction. The spectrum was similar to that observed in Pd/HZSM-5 (Si/Al$_2$ = 23.8), as given in the figure.[24] Therefore, the generation of Pd species similar to the Pd/HZSM-5 was suggested from the EXAFS measurement. Previously, we had observed that the oxidation of Pd was found to take place at around 623 K in the temperature-programmed oxidation of metal Pd loaded on HZSM-5 in an atmosphere of O$_2$.[25] In the present case of Pd/HPW/SiO$_2$, Pd was found to be already oxidized at 473 K. The temperature was lower than that observed on Pd/HZSM-5 by 150 K. Therefore, it was supposed that the strong Brønsted acid sites in HPW promoted the oxidation of Pd. Similar phenomena were observed in Pd loaded on zeolites or metal oxide supports with a different character, where the acid property of the support promoted the generation of PdO.[26,27] Probably, acidic supports with electrophilic character resulted in stabilization of the electron-deficient character of Pd. Thus, the Pd surface was easily oxidized. Taking this fact into consideration, one of the reasons for the characteristic activity of Pd at low temperature over HPW was ascribed to the ready formation of dispersed PdO that promoted the redox cycle of the Pd center. In the EXAFS spectrum measured after the reaction above 723 K, a broad peak appeared at 0.30 nm, which could be attributed to the Pd–(O)–Pd bond of agglomerated PdO. Thus, the appearance of the peak suggested the formation of sintered PdO. At this temperature, the activity of Pd was already reduced, as shown in Fig. 1. Probably, the destruction of the Keggin structure of HPW promoted the sintering of PdO caused by water vapor. Thereby, the activity of Pd decreased at high temperature.

Figure 9 shows the EXAFS Fourier transforms of the W L$_3$-edge of Pd/HPW/SiO$_2$ measured before and after the reaction at different temperatures. Three peaks ascribed to the W=O, W–O, and W–O–W of the Keggin structure were observed at 0.13, 0.16, and 0.33 nm in the Fourier transforms, respectively. No change was observed in the spectra collected after the reaction up to 673 K, indicating that the Keggin structure of HPW was preserved over the temperature range. However, a significant change was found above 773 K, where W–O and W–O–W bonds appeared at 0.14 nm and 0.33 nm, respectively. Probably, the change meant the decomposition of HPW into P$_2$O$_5$ and WO$_3$ at high temperature.[28] From the data of W L$_3$-edge EXAFS spectra, the Keggin structure of HPW was confirmed to be retained at 473–623 K in which the catalyst exhibited activity in the NO reduction.

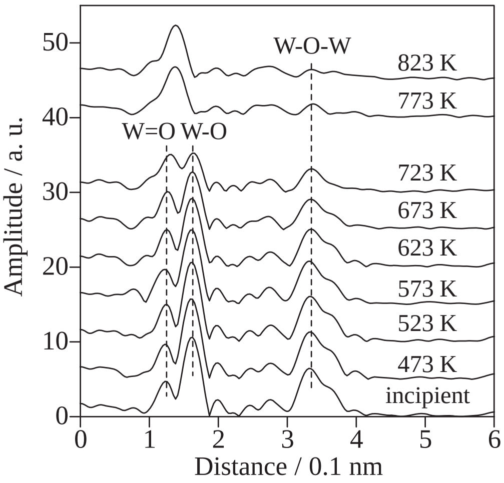

Fig. 9. W L$_3$-edge EXAFS Fourier transforms of Pd/HPW/SiO$_2$ catalysts measured before and after the catalytic reaction for 3 h at different temperatures. Pd loading, 0.2 wt %; HPW loading, 20 wt %.

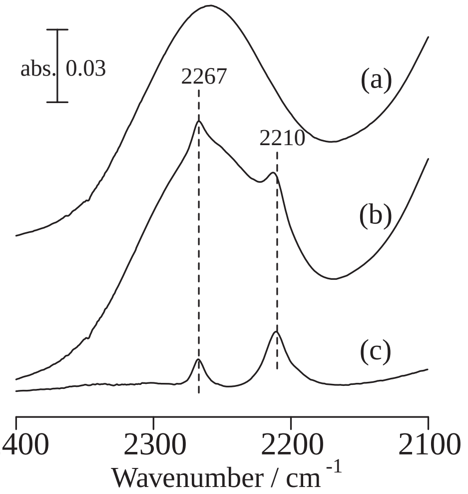

Fig. 10. IR spectra of Pd/HPW/SiO$_2$ measured (a) pretreated at 473 K (b) after reaction in the gas mixture of NO 1000 ppm, CH$_4$ 1000 ppm, O$_2$ 1%, He balance and (c) subtracted spectrum. Pd loading, 1.0 wt %; HPW loading, 30 wt %.

IR Measurement of Adsorbed NO. In order to investigate the adsorbed species of NO present in the Pd/HPW/SiO$_2$ catalyst, IR spectra were measured after the reaction at 473 K for 4 h in a gas flow of NO–CH$_4$–O$_2$–(10% H$_2$O). Measurements were undertaken after a replacement of the flowing gas with He, followed by cooling down to room temperature. Figure 10 gives IR spectra measured before and after the reaction. In comparison with the spectrum measured before the reaction, novel peaks appeared at 2210 and 2267 cm^{-1} after the reaction at 473 K. In the studies concerning the adsorption of NO into HPW, McCormick assigned a peak appearing at 2267 cm^{-1} to the N=O bond of N–OH$^+$.[29] The peak at 2210 cm^{-1} was assigned to highly strained δ(O–H), although the authors commented that a further confirmation was necessary. Taking these assignments into account, probably the appearance of these peaks indicated the formation of N–OH^+ species during the reaction.[11,30,31] It has been reported that NO was strongly adsorbed in the "pseudoliquid" phase of HPW.[32] The adsorption of NO takes place through a displacement of NO with a water molecule present in the secondary structure of HPW. Although the amount and the rate of NO uptake were suppressed when HPW was loaded on SiO_2, still a similar adsorbed species of NO was observed on HPW/SiO_2.[29] In the present catalyst, the formation of similar N–OH^+ species in Pd/HPW/SiO_2 was confirmed from the IR spectra. Probably, the enrichment of NO in the secondary structure of the Keggin structure and the activation of NO caused by H^+ gave rise to the NO reduction activity at low temperature over a Pd/HPW/SiO_2 catalyst.

Conclusion

The selective reduction of NO with methane was carried out over Pd loaded on a HPW/SiO_2 catalyst. It was found that the catalyst exhibited activity at around 523 K. The temperature was significantly lower than that of conventional Pd based catalysts. The addition of water vapor was effective to improve the catalytic activity. Probably, the reason for the characteristic activity was due to the strong adsorption and activation of NO in the secondary structure of $H_3PW_{12}O_{40}$, in addition to the readily formation of dispersed PdO species over the HPW supports.

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