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Pd loaded on high silica beta support active for the total oxidation of diluted methane in the presence of water vapor

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Abstract

Total oxidation of diluted methane was carried out over palladium loaded on H-beta and H-ZSM-5 having different Al concentration in order to reveal the support effect of zeolites. It was found that the Al concentration had significant influence on the methane combustion activity of Pd. Especially, Pd loaded on H-beta having the lowest concentration of Al exhibited the most striking performance in that it showed superior durability and the highest activity in the presence of 10% water vapor. In marked contrast to the zeolite-supported Pd catalysts, Pd loaded on SiO_2 was substantially inactive under the same reaction conditions. Based on the Pd K-edge EXAFS coupled with TG analysis, the reason for the superior nature of high silica H-beta was attributed to the hydrophobic character of supports and the formation of agglomerated PdO, which was active in the methane combustion.

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1. Introduction

Catalytic combustion of methane has been attracted much attention from the viewpoint of power production without the formation of thermal NO_x and the elimination of trace methane included in the exhaust gas, which cause the severe greenhouse effect [1–3]. Palladium is the most active catalyst in the total oxidation of methane among transition metal catalysts. It has been found that the active Pd species depends remarkably on the reaction conditions and the kind of supports. That is to say, PdO is an active component for methane combustion in the oxygen-rich conditions [4,5], while metal Pd participates in the reaction under reductive conditions [6–10]. In addition to the reaction conditions, the catalytic performance as well as the structure of Pd varies significantly depending on the kind of support. In the previous reports, alumina and zirconia have been favorably employed as supports for Pd. However, in many cases the activity of Pd loaded on these supports declined with duration of time in the presence of water vapor existed in the feed gas or generated along with methane combustion. Such deactivation was considered to be caused by gradual sintering of Pd species [11] or the formation of $Pd(OH)_2$ generated by the hydrolysis of PdO, which was inactive in the methane combustion. Recently, several research groups tried to employ SiO_2 as an alternative support for Pd. Pd loaded on SiO_2 was found to be relatively tolerant to the water vapor because of the hydrophobicity of support as demonstrated by Araya et al. [12]. They claimed that the hydrophobic character of SiO_2 was an important factor in the tolerance of Pd support against water vapor. Indeed, the apparent reaction order with respect to water was -0.25 over Pd/SiO_2, while the order was measured to be -1 over Pd/Al_2O_3 or Pd/ZrO_2. Burch also pointed out that the partial pressure of water in the neighborhood of active surface of PdO affected the catalytic activity [13].

In the present study, H-beta and H-ZSM-5 zeolites were employed as support for Pd. The regular pore structure of zeolites was expected to be beneficial for Pd to remain in the hydrophobic environment [14]. Another advantage of zeolite was that the acid property could be readily tuned by changing the Al concentration. This is important considering the Al concentration was the key factor in the regulation of the size of Pd. As a matter of fact, the size of Pd was considerably dependent on the concentration of acid sites of zeolite. That is to say, the atomically dispersed PdO was stabilized on the

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zeolites with high acid concentration, whereas the agglomerated PdO generated on the zeolites with lower acid concentration [15,16]. The fact meant that the size of PdO could be regulated through the concentration of acid sites of zeolites. To this end, 0.1 wt% Pd was loaded on H-beta and H-ZSM-5 zeolites with different Al concentration. The loading of Pd with low concentration (0.1 wt%) aimed at the emphasis on the support effect of zeolites. The catalytic performance in the methane combustion was correlated with the hydrophobicity of support and structure of Pd characterized by means of EXAFS. EXAFS is a powerful tool for investigation of the local structure of a given element. Although, the concentration of Pd in the present sample was extremely low, the measurement was possible with the use of a brilliant X-ray source together with the small X-ray absorption coefficient of zeolite matrix enough to detect the signal of Pd at the energy range of Pd K-edge (24.3 keV) [17].

2. Experimental

2.1. Catalysts preparation

H-ZSM-5 with $Si/Al_2 = 23.8$ and 90 were supplied from Tosoh Co. and The Catalysis Society of Japan (JRC-Z5-90H), respectively. H-ZSM-5 samples with lower Al concentrations were prepared with hydrothermal synthesis according to the procedure reported previously [18]. In brief, tetrapropylammonium bromide (Wako), sodium silicate (nakalai tesque), aluminum sulfate (Wako) were used as a template, silica source, aluminum source, respectively. The synthesis was carried out at 443 K for 72 h using an autoclave. The template of the as-made ZSM-5 was removed by calcination in an N_2 flow, followed by oxidation in an O_2 flow at 813 K. Finally, H-form of ZSM-5 was obtained by ion-exchange with a 0.5 M NH_4NO_3 solution, followed by calcination in an N_2 flow at 773 K.

H-beta having different Al concentration was prepared by the dealumination of H-beta supplied from PQ Co. ($Si/Al_2 = 25$), as a source material. The dealumination was carried out with an oxalic acid (Wako) solution according to the literature [19]. The Al content of H-beta was regulated by changing the concentration of an oxalic acid solution, temperature and the time for dealumination. The structure of H-beta and H-ZSM-5 was characterized by means of XRD prior to the loading of Pd. Fig. 1 shows the XRD patterns of the zeolites employed as supports for Pd. The diffraction patterns characteristic of each zeolite was confirmed in the figures, indicating that the crystal structure of BEA or MFI was retained in the samples used here.

Pd was loaded on H-ZSM-5 and H-beta by an ion-exchange method using $Pd(NH_3)_4Cl_2$ (Aldrich) as a precursor. The ion-exchanged sample was calcined in an N_2 flow, followed by an O_2 flow at 773 K. The loading of Pd was 0.1 wt% as analyzed with ICP. As a comparable experiment, 0.1 wt% Pd was loaded on SiO_2 (Wako Chemical) by an impregnation method using $Pd(NH_3)_4Cl_2$ as a precursor. The subsequent treatments were carried out in a manner similar to the preparation of zeolite-supported Pd catalysts.

2.2. Catalytic reaction

Methane combustion was carried out with a continuous fixed bed reactor. A gas mixture of methane (2000 ppm) diluted with N_2 and 10% O_2 (total flow rate, 100 ml min^{-1}) was fed into a Pyrex glass reactor under atmospheric pressure. Water was fed into the reactor with a microfeeder. Water was vaporized at the inlet of the reactor, and then mixed with the reactant gas mixture. A 50 mg of catalyst mixed with glass beads (1 g) was used for the reaction. An effluent gas was analyzed with a gas chromatograph (Shimadzu GC-8A) equipped with a TCD detector. Molecular Sieves 13X and Porapak Q columns were used to separate the gas mixture.

2.3. EXAFS measurement and analysis

Pd K-edge (24.3 keV) EXAFS data were collected at BL01B1 station in the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2004B0311-NXa-np). A Si(1 1 1) single crystal was used to obtain a monochromatic X-ray beam. The beam size was 1 mm × 5 mm at the sample position. The measurement was carried out under ambient condition. The energy of X-ray was calibrated with a Pd foil as the reference. The Fourier transformation of the k^3-weighted EXAFS oscillation from k space to r space was performed over the range 25–120 nm^{-1} to

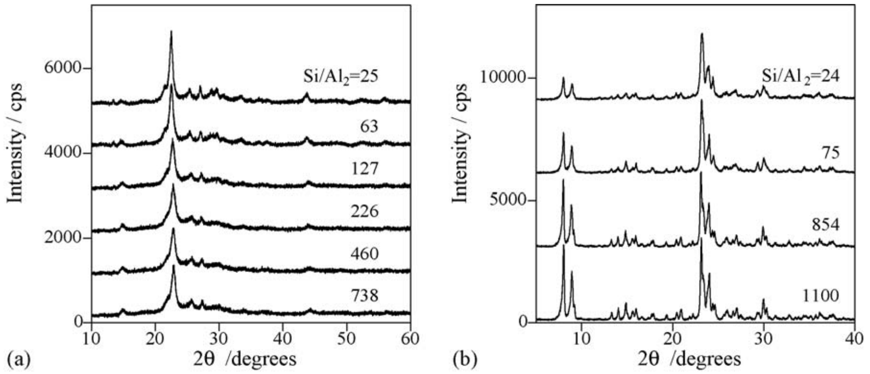

Fig. 1. Powder XRD patterns of (a) H-beta and (b) H-ZSM-5 with different Si/Al_2 ratios.

obtain a radial distribution function (Fig. 7). The inversely Fourier filtered data over the range of 0.21–0.38 nm was analyzed by a usual curve-fitting method. For the curve-fitting analysis, the empirical phase shift and amplitude functions for Pd–Pd were extracted from the data of Pd foil. The analysis of EXAFS data was conducted using the ‘‘REX2000, Ver. 2.0.7’’ program (Rigaku).

2.4. XPS analysis

X-ray photoelectron spectroscopy (XPS) was measured with the Omicron ESCA PROBE II spectrometer. Catalysts were calcined pretreated at 773 K for 1 h in O_2 and subsequent treatment with 10% water vapor at 773 K for 6 h. The pretreated samples were pressed into a wafer form and suspended on a sample mount. The charge compensation of the samples was controlled by referencing to the C 1s line at 284.8 eV.

3. Results and discussion

3.1. Catalytic reactions

The catalytic performance of 0.1 wt% Pd loaded on zeolites or SiO_2 were given in Fig. 2. Under the dry condition, Pd loaded on H-beta and H-ZSM-5 exhibited a similar tendency in that the activity increased with decreasing the Al concentration of zeolites (Fig. 2(a) and (c)). The light-off curve shifted to the higher temperature under 10% water vapor, meaning the activity declined considerably by the addition of water vapor (Fig. 2(b) and (d)). It was found from the comparison of the catalytic activity using H-beta and H-ZSM-5 supports that the Pd/H-beta exhibited higher activity in the presence of water vapor. In marked contrast with zeolite supports, Pd loaded on SiO_2 exhibited quite low activity. Namely, the methane conversion measured at 773 K was as low as 21% under dry condition and it became totally inactive in the presence of 10%

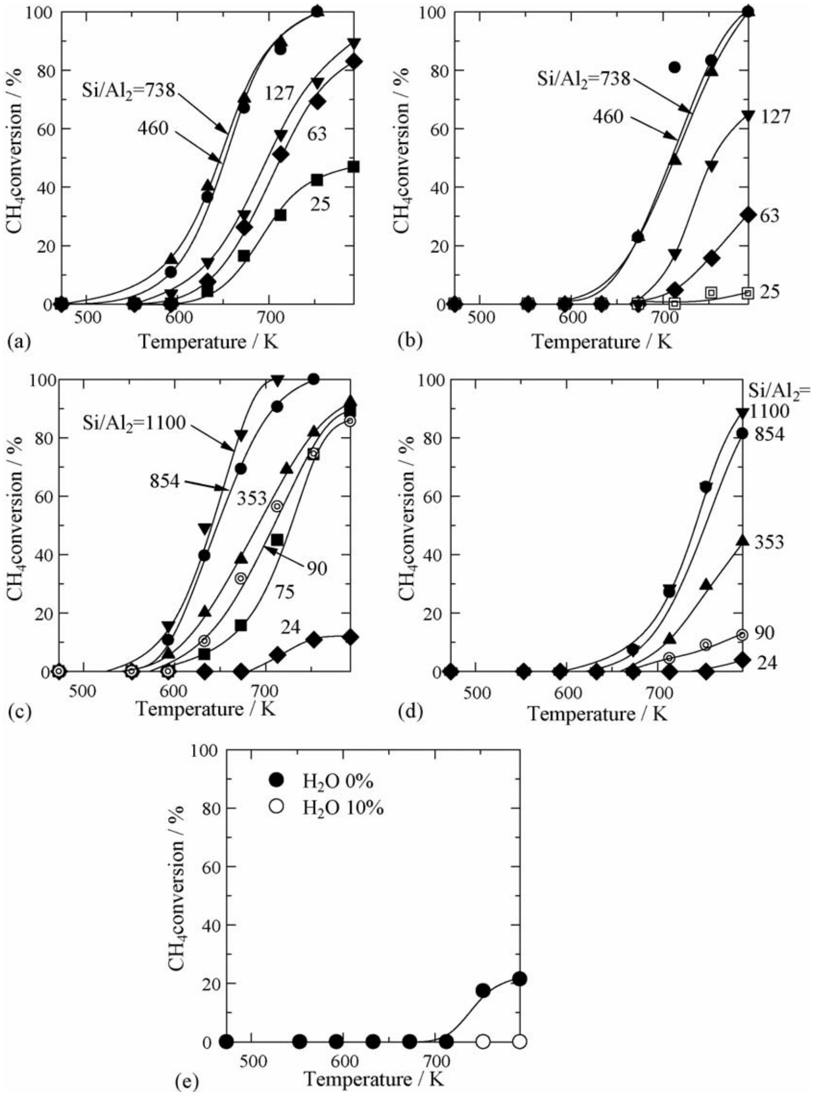

Fig. 2. Methane conversion plotted as a function of temperature: (a) Pd/H-beta under dry condition, (b) Pd/H-beta under 10% water vapor, (c) Pd/H-ZSM-5 under dry condition, (d) Pd/H-ZSM-5 under 10% water vapor and (e) Pd/SiO_2 under dry condition and 10% water vapor.

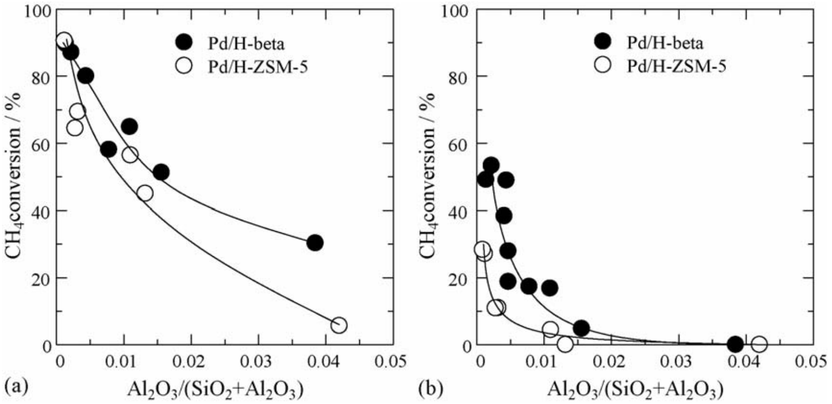

Fig. 3. Dependence of the CH_4–O_2 conversion on the Al concentration of H-beta and H-ZSM-5: (a) dry condition and (b) under the 10% water vapor. Pd loading, 0.1 wt%, temperature, 713 K.

water vapor. Thus, the superior nature of zeolite supports was recognized from the comparison with SiO_2.

Fig. 3 shows the methane conversion plotted as a function of Al concentration of zeolites (reaction temperature, 713 K). Pd loaded on H-ZSM-5 and H-beta showed similar curves under the dry condition. On these catalysts, the conversion of methane increased accompanied by decreasing the Al concentration of support. The overall activity was reduced by the addition of 10% water vapor. Especially, the conversion reduced to zero on the supports with higher concentration of Al. However, the extent of the suppression was smaller over the zeolites with lower Al concentration. As a result, the dependence of the Al concentration became sharp in the $Al_2O_3/(Al_2O_3 + SiO_2)$ range between 0 and 0.005. In this region, Pd loaded on H-beta exhibited higher activity in comparison with Pd/H-ZSM-5. It could be noted from these data that the H-beta with high silica composition was the most appropriate support for Pd in the methane combustion.

Fig. 4 gives the time-course change in the methane combustion activity measured in the 10% water vapor (temperature, 713 K). The methane conversion slowly declined with duration of time over Pd/H-ZSM-5, whereas Pd/H-beta exhibited stationary activity even after 6 h from the beginning of the reaction. Fig. 5 shows the time-course change in the methane conversion where 10% water vapor was repeatedly introduced to the reactor. Although, the conversion decreased by the addition of water vapor, it recovered completely by the switching-off the feed of the water vapor repeatedly, meaning the effect of water vapor was reversible upon the reaction. From these data, it could be noted that the Pd loaded on high silica H-beta possessed superior nature in that it exhibited high activity and durability in the methane combustion in the presence of water vapor.

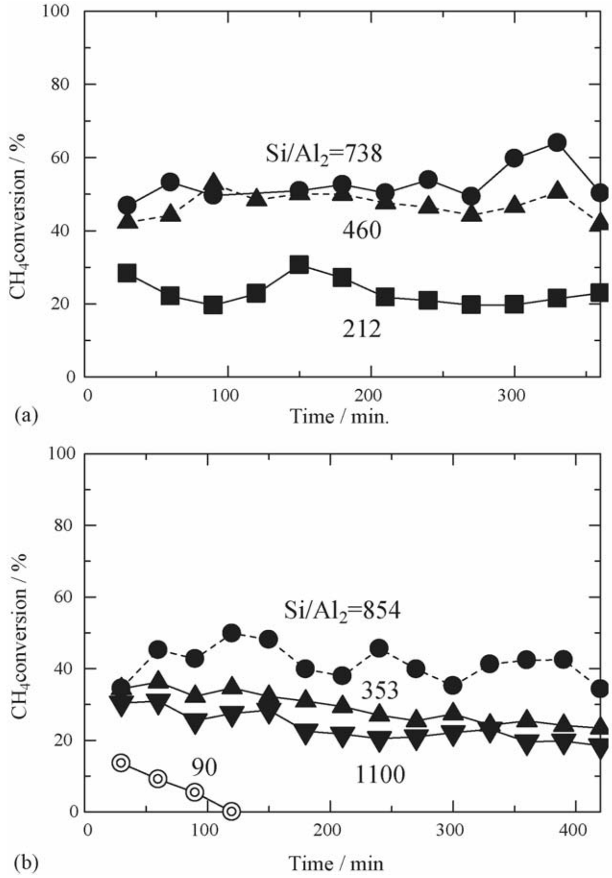

Fig. 4. Time-course change in the methane combustion activity in the 10% water vapor: (a) Pd/H-beta, (b) Pd/H-ZSM-5. Temperature, 713 K.

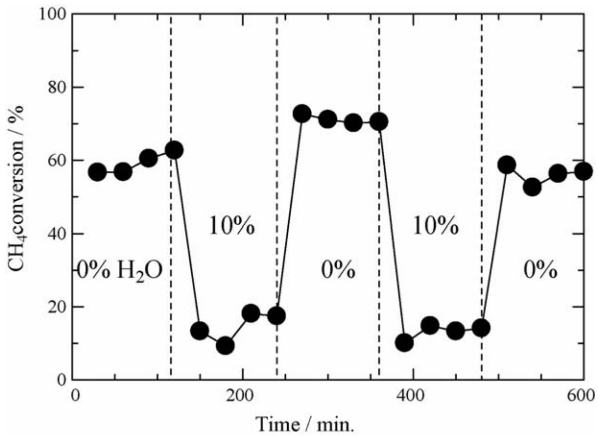

Fig. 5. Time-course change in the methane combustion activity of 0.1% Pd/H-beta ($Si/Al_2 = 738$), while 10% water vapor was added to the flowing gas repeatedly. Temperature, 673 K.

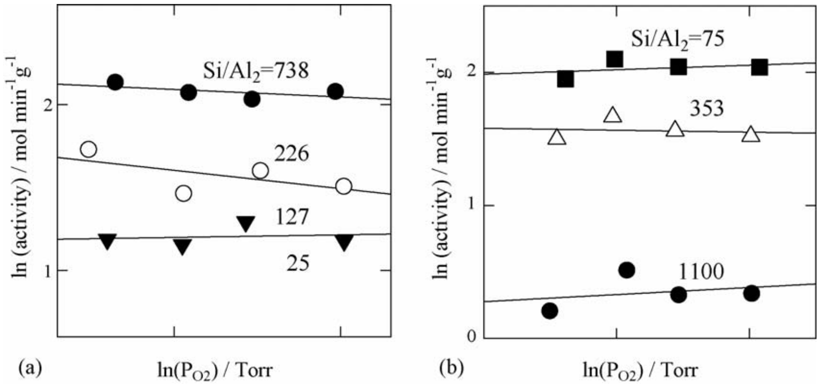

Fig. 6. Effect of partial pressure of O_2 on the methane combustion activity. (a) Pd/H-beta, (b) Pd/H-ZSM-5.

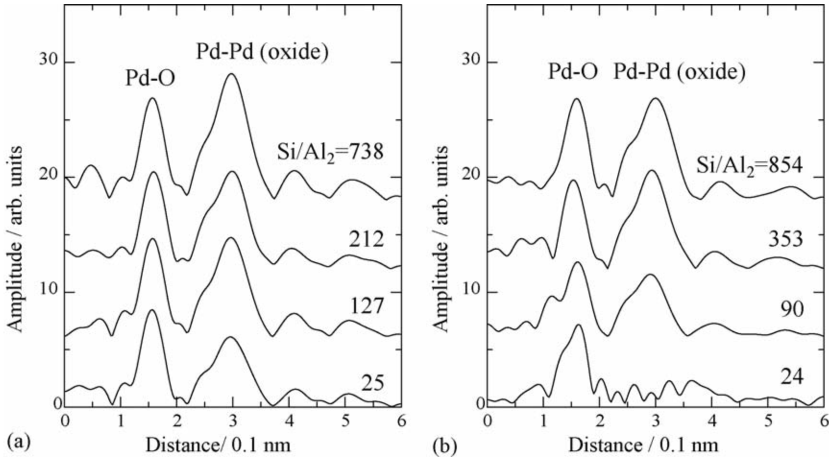

Fig. 7. Pd K-edge $k^3\chi(k)$ EXAFS Fourier transforms of 0.1 wt% Pd loaded on: (a) H-beta and (b) H-ZSM-5 measured after oxidation at 773 K. Fourier transform range, 25–120 nm^{-1}.

Fig. 6 shows the effect of O_2 partial pressure on the methane combustion activity. The reaction order with respect to O_2 pressure was almost zero independent of the zeolite structure and Al concentrations, implying the active phase was ascribed to the PdO. This is because the zero order against O_2 pressure meant that the surface of the Pd was fully covered with oxygen atoms. On the other hand, the reaction order with respect to the H_2O vapor pressure was measured to be −0.48 to −0.76 and −0.58 to −0.87 over H-beta and H-ZSM-5, respectively. The value was higher than the −1 order typically reported for Pd/Al_2O_3 [20].

3.2. Characterization of Pd loaded on H-beta and H-ZSM-5

Fig. 7 shows Pd K-edge EXAFS Fourier transforms of 0.1 wt% Pd loaded on H-beta and H-ZSM-5 measured after the calcination in O_2 at 773 K. Two intense peaks attributed to the Pd–O and Pd–Pd bonds of PdO appeared at 0.16 and 0.30 nm (phase shift uncorrected), respectively. The Pd–Pd peak was comprised of the contribution from two kinds of Pd–Pd bonds (cf. the Pd–Pd bonds of bulk PdO were CN = 4, distance = 0.304 nm; CN = 8, distance = 0.342 nm). The intensity of Pd–Pd bonds increased accompanied by decreasing the Al

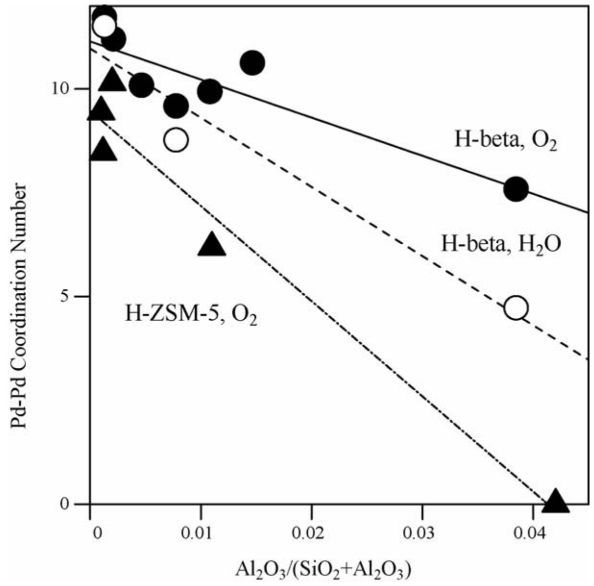

Fig. 8. Coordination numbers of Pd–Pd bonds calculated based on Pd K-edge $k^3\chi(k)$ EXAFS Fourier transforms of 0.1 wt% Pd loaded on H-beta and H-ZSM-5 oxidized at 773 K or treated with 10% water vapor at 773 K for 3 h.

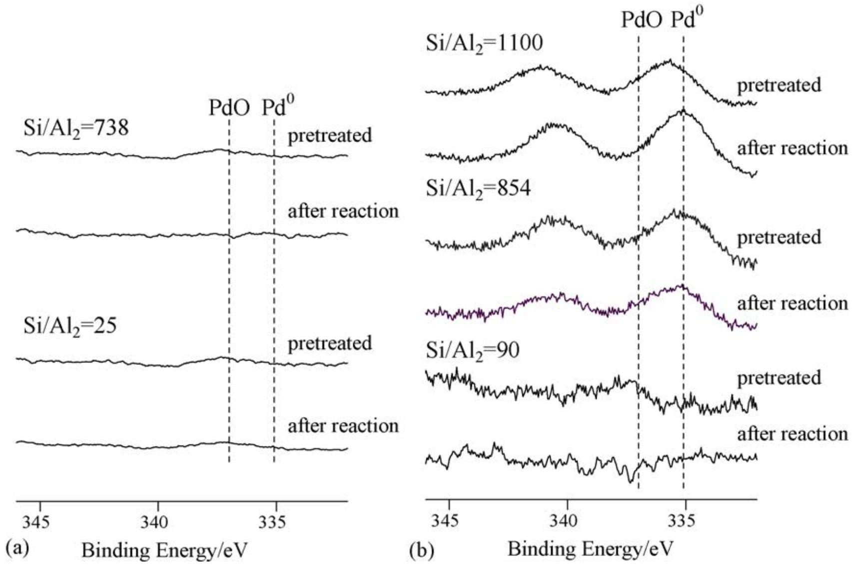

Fig. 9. Pd 3d XPS of: (a) Pd/H-beta and (b) Pd/H-ZSM-5 oxidized at 773 K and after reaction under 10% water vapor at 713 K for 6 h.

concentration. The change meant the generation of PdO with larger size on zeolites with low Al concentration. The coordination numbers (CNs) of the two kinds of Pd–Pd bonds were determined by the curve-fitting analysis and the sum of the CNs is displayed in Fig. 8. One can see that the CNs of Pd loaded on ZSM-5 and H-beta commonly increased with decreasing the concentration of Al. The CNs of Pd/H-beta was larger than that of Pd loaded on H-ZSM-5 when the comparison was made at a given Al concentration, implying the formation of PdO with larger size on the H-beta support. The generation of agglomerated PdO may be caused by weakening the interaction between PdO and acid sites present in H-beta. As a matter of fact, in the energy-dispersive EXAFS studies concerning Pd loaded on H-ZSM-5, we found that the acid–base interaction between acid sites of zeolite and PdO promoted the spontaneous formation of highly dispersed PdO; the reversible transformation between dispersed PdO and the agglomerated metal Pd was observed in the atmospheres of O_2 and H_2, respectively [15,21]. Probably, the weak acid strength of H-beta in comparison with H-ZSM-5 was responsible for the formation of PdO with larger size in the micropore of H-beta. The value of CNs of Pd–Pd increased to 9.5–11.5 in the Al_2O_3/(SiO_2 + Al_2O_3) ratio less than 0.015. At this Al concentration region, the Pd/H-beta exhibited the highest activity in the methane combustion. The particle size effect of PdO observed here was evidenced by Hicks et al. and Burch et al. using Pd/Al_2O_3 catalysts [22–24]. For example, Hicks et al. reported that the methane combustion activity of dispersed PdO was 10–100 times lower than that of the small palladium crystallites. The low activity of PdO with dispersed form was explained through the difficulty in the generation of oxygen vacancy [25].

XPS data of the Pd/H-ZSM-5 and H-beta was recorded after the treatment with O_2 or methane combustion conducted in the presence of 10% water vapor at 713 K in order to characterize the Pd species present on the external surface of zeolites (Fig. 9). The peaks ascribed to be Pd 3d peaks were observed over Pd loaded on H-ZSM-5 with Si/Al_2 = 854 and 1100, meaning a part of Pd was present on the external surface of these H-ZSM-5 zeolites. The peak position was close to that of metal Pd regardless of the treatments. Probably, the metal Pd detected by XPS was not directly related with the reaction, since the metal Pd itself was generally considered to be inactive in the methane combustion [26]. In addition, the quantity of the metal Pd present in H-ZSM-5 detected by XPS was expected to be negligible taking into account that palladium oxide was observed as a sole component in EXAFS data. On the other hand, no signal was detected over Pd/H-beta. Therefore, it was considered that the agglomerated PdO in Pd/H-beta was not present on the external surface of H-beta.

Fig. 10 gives the water content in H-beta and H-ZSM-5 measured by means of thermogravimetry (TG) analysis. The samples were placed in the atmosphere of 80% humidity

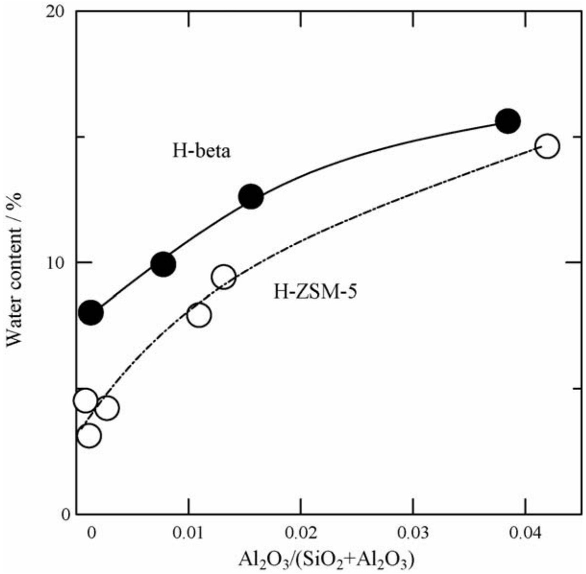

Fig. 10. Water content determined based on the TG data plotted against Al concentration of H-beta and H-ZSM-5 zeolites.

overnight prior to the measurement. The water content decreased accompanied by decreasing the Al concentration of zeolites. The tendency agreed well with the catalytic performance in that the methane combustion activity sharply increased in the high silica region in the presence of water vapor. It has been proposed that the deactivation of PdO was caused by the hydration of the PdO forming $Pd(OH)_2$ phase in the presence of water produced accompanied by the reaction [27,28]. The dissociation of methane was suppressed over $Pd(OH)_2$. Although, the bulk $Pd(OH)_2$ decomposed at 523 K in the atmosphere of N_2, the $Pd(OH)_2$ phase was stabilized at high temperature under the presence of excess water [29,30]. Taking these facts into account, it could be supposed that the formation of $Pd(OH)_2$ was hindered by the hydrophobic character of high silica H-beta. Thus, the other effect of high silica composition may be ascribed to the enhancement of the hydrophobic character of support accompanied by decrease in the Al concentration.

4. Conclusions

Total oxidation of diluted methane was carried out over Pd loaded on zeolites with MFI and BEA structure. The high activity in the methane combustion and the tolerance to the water vapor was realized over the zeolites with low Al concentration. Especially, Pd loaded on H-beta zeolite having high silica composition exhibited excellent activity. The influence of water vapor on Pd/H-beta was reversible upon the repeated admission of water vapor. The reasons for superior nature of Pd/H-beta support with low Al concentration were attributed to the hydrophobic character of support and the formation of agglomerated PdO, which was active in the methane combustion.

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References

[1] D.E. Resasco, Y.-H. Chin, Total oxidation of methane on Pd catalysts, in: Catalysis: Specialist Periodical Reports, vol. 14, The Royal Society of Chemistry, London, 1999, p. 1.
[2] P. Gelin, M. Primet, Appl. Catal. B 39 (2002) 1.
[3] T. Choudhary, S. Banerjee, V. Choudhary, Appl. Catal. A 234 (2002) 1.
[4] R.F. Hicks, H. Qi, M.L. Young, R.G. Lee, J. Catal. 122 (1990) 280.
[5] P. Briot, M. Primet, Appl. Catal. 68 (1991) 301.
[6] K. Okumura, S. Matsumoto, N. Nishiaki, M. Niwa, Appl. Catal. B 40 (2003) 151.
[7] J.N. Carstens, S.C. Su, A.T. Bell, J. Catal. 176 (1998) 136.
[8] M. Lyubovsky, L. Pfefferle, Appl. Catal. A 173 (1998) 107.
[9] M. Lyubovsky, L. Pfefferle, Catal. Today 47 (1999) 29.
[10] A.K. Datye, J. Bravo, T.R. Nelson, P. Atanasova, M. Lyubovsky, L. Pfefferle, Appl. Catal. A 198 (2000) 179.
[11] K. Muto, N. Katada, M. Niwa, Appl. Catal., A 134 (1996) 203.
[12] P. Araya, S. Guerrero, J. Robertson, F.J. Gracia, Appl. Catal. A 283 (2005) 225.
[13] R. Burch, Catal. Today 35 (1997) 27.
[14] H. Maeda, Y. Kinoshita, K.R. Reddy, K. Muto, S. Komai, N. Katada, M. Niwa, Appl. Catal. A 163 (1997) 59.
[15] K. Okumura, M. Niwa, J. Phys. Chem. B 104 (2000) 9670.
[16] K. Okumura, M. Niwa, Catal. Surv. Jpn 5 (2002) 121.
[17] K. Okumura, J. Amano, N. Yasunobu, M. Niwa, J. Phys. Chem. B 104 (2000) 1050.
[18] J.H. Kim, T. Kunieda, M. Niwa, J. Catal. 173 (1998) 433.
[19] M. Bjørgen, S. Kolboe, Appl. Catal. A 225 (2002) 285.
[20] F.H. Ribeiro, M. Chow, R.A. Dalla Betta, J. Catal. 146 (1994) 537.
[21] K. Okumura, R. Yoshimoto, T. Uruga, H. Tanida, K. Kato, S. Yokota, M. Niwa, J. Phys. Chem. B 108 (2004) 6250.
[22] R.F. Hicks, H. Qi, M.L. Young, R.G. Lee, J. Catal. 122 (1990) 280.
[23] R.F. Hicks, H. Qi, M.L. Young, R.G. Lee, J. Catal. 122 (1997) 295.
[24] T.R. Baldwin, R. Burch, Appl. Catal. 66 (1990) 337.
[25] R.S. Weber, J. Catal. 151 (1995) 470.
[26] R. Burch, F.J. Urbano, Appl. Catal. A 124 (1995) 121.
[27] C.F. Cullis, T.G. Nevell, D.L. Trimm, J. Chem. Soc., Faraday Trans. 1 (1972) 1406.
[28] D. Roth, P. Gélin, M. Primet, E. Tena, Appl. Catal. A 203 (2000) 37.
[29] R.J. Card, J.L. Schmitt, J.M. Simpson, J. Catal. 79 (1983) 13.
[30] R. Burch, F.J. Urbano, P.K. Loader, Appl. Catal. A 123 (1995) 173.