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Role of zeolite structure on reduction of NO_x with methane over In- and Pd-based catalysts

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Abstract

Catalytic performances of ZSM-5 based catalysts containing indium or palladium were examined for NO reduction with CH_4 and NO_x chemisorption. The amounts of NO_x chemisorbed on In/H-ZSM-5 were well proportional to the catalytic activities for NO_x reduction. Pd/H-ZSM-5, on the other hand, hardly chemisorbed NO_2, while the catalytic activity for NO_2 reduction with CH_4 is very high. Furthermore, Pd loaded on SiO_2 showed comparably high catalytic activity for NO_2 reduction with CH_4 at 400°C in the absence of oxygen as Pd/H-ZSM-5. CH_4 combustion during NO_x reduction with CH_4 in the presence of oxygen significantly occurred over PdO on SiO_2, while less over Pd/H-ZSM-5. The role of zeolite might be slightly different between In/H-ZSM-5 and Pd/H-ZSM-5: the zeolitic porous structure is needed for In/H-ZSM-5 in order to concentrate NO_2 adspecies on InO^+ sites, which is important for NO reduction with CH_4 on In/H-ZSM-5 based catalysts, while the ion-exchangeable ability of zeolite is needed for Pd/H-ZSM-5 in order to make Pd^{2+} located in a highly dispersed state, on which NO is strongly chemisorbed. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: NO_x reduction; Methane; Zeolite; Indium; Palladium

1. Introduction

Reduction of nitric oxide with hydrocarbons has been focused on for the substitute of the $deNO_x$ catalysis such like NH_3-SCR. Many catalysts, in particularly, zeolite-based catalysts have been reported to be high active and selective for this reaction [1–8]. However, the role of zeolite structure on this reaction is in dispute. If we can get more information about that, the catalysts having much higher activity and selectivity will be expected.

Recently, many researchers have been stimulated to create high catalysis by combination of the catalytic sites for NO oxidation and NO reduction [9–16]. Among them, interesting results have been reported by Misono et al. on Mn_2O_3/Sn-ZSM-5 [15]. They have claimed that the catalytic activity of Mn_2O_3/Sn-ZSM-5 was enhanced by H_2O, because the deposition of carbonaceous materials was suppressed by the coexistence of H_2O. Another interesting catalytic process has recently been found by Iwamoto et al. [16]. They introduced hydrocarbon as a reductant into the reactant feed between the catalytic beds of NO oxidation and NO_x reduction, which has been named "Intermediate Addition of Reductant (IAR)" method. Therefore, bifunctional catalysis must be indispensable for the design of much higher catalysis.

We have also reported that the catalytic activities for NO reduction with CH_4 on In/H-ZSM-5 and Pd/H-

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ZSM-5 were promoted by the addition of NO oxidation sites, such as Ir and Co, respectively [9–13]. As for Ir/In/H-ZSM-5, the property of zeolite porous structure is effective as "intrapore catalysis": NO oxidation and NO_2 reduction with CH_4 on Ir and InO^+, respectively, occurs in an identical pore of zeolite [12].

The aim of this paper is to discuss about the role of zeolite for the catalytic activities of NO reduction with CH_4 using In/H-ZSM-5 and Pd/H-ZSM-5.

2. Experimental

Na-ZSM-5 zeolites (SiO_2/Al_2O_3 molar ratio of 23.8 and 39.4) were supplied by Tosoh. In/H-ZSM-5 were prepared by ion exchange of NH_4-ZSM-5 derived from the Na-type with aqueous solutions of nitrate at 95°C for 24 h, followed by calcination at 540°C for 3 h. The level of indium content was 4.0 wt%. Pd/H-ZSM-5 catalyst with a 0.4 wt% Pd loading was prepared by the ion exchange method: NH_4-ZSM-5 was ion-exchanged by stirring in a solution of $Pd(NH_3)_4Cl_2$, being adjusted at pH 10 with 7% NH_4OH at room temperature for 2 h, followed by filtration and washing with decationized water. Pd/SiO_2 was prepared by impregnation of SiO_2 in palladium nitrate solution. Pd catalysts were dried at 110°C overnight and were changed into H-type of ZSM-5 by heat treatment prior to reaction. The chemical composition of the catalysts were determined by means of ICP. Pd/H-ZSM-5 and Pd/SiO_2 having 0.4 wt% Pd were used as the standard catalysts for kinetic studies.

Reduction of NO_x and oxidation of NO were carried out in a fixed-bed flow reactor, by feeding a mixture of 100–1000 ppm NO_x, 1000 or 2000 ppm CH_4, 10% O_2, and 10% H_2O in He balance at a rate of 100 cm^3 min^{-1} to 0.1 or 0.25 g catalyst. Kinetic studies employed higher GHSV to obtain low levels of NO_x conversion below 40%. Water vapor was admitted by passing He through a saturator heated in water bath controlled at 60°C, and the wet He was mixed with other reactants. The reactant stream-line was heated at 100°C to avoid H_2O condensation. Catalysts were pretreated in a 20% O_2/He stream at the rate of 5°C/min to 500°C and held at 500°C for 1 h prior to reaction. Effluent gases were analyzed using a gas chromatograph and a chemiluminescence NO_x analyzer. Catalytic activities were evaluated by the level of NO_x conversion to N_2.

Infrared spectra were recorded with a Valor-III (JASCO) FT-IR spectrometer, connected to a diffuse-reflectance IR cell using a KBr window by passing a reactant gas mixture of 1000 ppm NO, 1000 ppm CH_4, and 10% O_2 in He at a rate of 100 cm^3(STP) min^{-1} over catalysts. 30 mg of a catalyst sample was set in a sample cup holder, and before recording a spectrum, the sample was heated up to 500°C at 5°C/min, calcined in an O_2 stream for 30 min, and then cooled to each reaction temperature. A spectrum was measured as a background before analysis of adspecies from NO_x–O_2 with or without CH_4 on the sample at each temperature. The spectra were collected with a resolution of 4 cm^{-1}.

The surface states of Pd species were studied by X-ray photoelectron spectroscopy (XPS). Spectra of Pd 3d was recorded with JPS90MX (JEOL). Monochromated Mg K_α radiation (1254 eV) was used for the measurements. The sample was pressed into a disk, set into the XPS sample holder, and outgassed to 1.0×10^{-8} Torr before each measurement. The 1s level of adventitious carbon (atmospheric hydrocarbons and surface carbon oxides) was taken as the internal reference, with the peak position at 285.0 eV.

Chemisorption of NO_x was measured by the pressure swing adsorption method reported in [12] under the same conditions as those for reaction, using the same gas mixture as that for reaction excluding CH_4 and H_2O. The concentration of NO_x passing through the catalyst bed was detected using a NO_x analyzer (NOA-305 A, Shimadzu). The amount of adsorbed NO_x was calculated from a breakthrough curve. The curve through a catalyst was measured till the slope of the curve was below 5 mmol s^{-1}. The reactor used in this measurement was made of a quartz tube with a 8 mm diameter and 25 cm long filled with glass beads to reduce dead volume, and NO_x adsorption did not completely occur in the absence of catalyst at the temperature tested. Catalysts were pelletized and crushed into 32–60 mesh size to reduce the pressure drop in the catalyst bed. A time lag was not so significant that the amount of chemisorbed NO_x can be calculated within the experimental error.

3. Results and discussion

Fig. 1 shows the catalytic activities of In/H-ZSM-5 and Pd/H-ZSM-5 for NO–CH_4–O_2 and CH_4–O_2 reactions. On In/H-ZSM-5, the light-off temperature of NO–CH_4–O_2 is lower than that of CH_4–O_2. It has already been reported [4] that NO hardly reacted with CH_4 in the absence of O_2 on In/H-ZSM-5; therefore NO_2 is involved in the reaction mechanism of this catalyst. Pd/H-ZSM-5, on the other hand, catalyzed CH_4–O_2 reaction from the identical temperature with NO–CH_4–O_2. It is interesting to note that CH_4 conversion was lower when NO is involved in the reactant feed. This indicates that NO significantly suppresses CH_4 combustion on Pd/H-ZSM-5.

To investigate the chemisorption of NO_x under the reaction conditions, the reactant without CH_4 was fed and the amount of chemisorbed NO_x was measured by use of pressure swing adsorption method [11]. Fig. 2 shows that the amount of NO_x chemisorbed and the catalytic activities for NO_x reduction on In/H-ZSM-5 and Pd/H-ZSM-5. Note that H_2O did not affect the series of the catalytic activities on both catalysts. NO was hardly chemisorbed on In/H-ZSM-5. It has previously reported that NO_2 was chemisorbed on InO^+ sites, and that the amounts of NO_x chemisorbed were well proportional to the catalytic activities of In/H-ZSM-5 based catalysts [12]. It means that the chemisorbed NO_2 is important adspecies for NO reduction with CH_4 on In/H/ZSM-5. Pd/H-ZSM-5, on the other hand, chemisorbed NO. The amount of NO chemisorbed on Pd/H-ZSM-5 decreases with O_2, and furthermore, the amount of chemisorbed NO_2 was less than that of NO on this catalyst. It is noted that there is no correlation between the amount of chemisorbed NO_x and the catalytic activities for NO_x reduction on Pd/H-ZSM-5. Several researches have claimed that NO reduction with CH_4 proceeds via the formation of NO_2 [13,17]. Therefore, it is considered that NO_2 rapidly reacts with CH_4 on Pd/H-ZSM-5, although it cannot be concluded which is the more reactive state of NO_2 with CH_4 whether in the gas phase or on the catalyst under the reaction conditions.

Fig. 3 shows the in-situ FT-IR spectra of In/H-ZSM-5 and Pd/H-ZSM-5 during NO reduction with CH_4 at 350°C. It is apparent that NO_2 adspecies on InO^+ sites were observed at 1619 and 1575 cm^{-1} on In/H-ZSM-5 even under the reaction conditions. These bands are assigned to the NO_2 adspecies on InO^+ sites [18]. This means that the rate-determining step for NO reduction with CH_4 on In/H-ZSM-5 is the reaction between NO_2 adspecies and CH_4 in the gas phase. Pd/H-ZSM-5, on the other hand, showed no intense peak except at 1910 cm^{-1}. This peak is assigned to NO adspecies, according to the literature [19], on Pd sites. NO_2 adspecies on Pd site, which can be seen at around 1630 cm^{-1}, was hardly observed, and one weak peak at 1570 cm^{-1} is attributed to NO_2 adspecies on H^+ sites. From these results, it is considered that NO adspecies on Pd sites might play an important role on NO reduction with CH_4 on Pd/H-

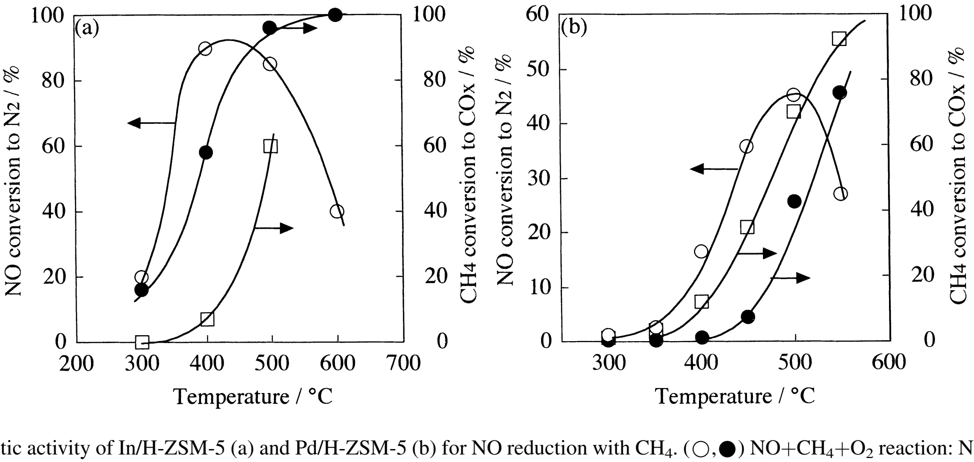


Fig. 1. Catalytic activity of In/H-ZSM-5 (a) and Pd/H-ZSM-5 (b) for NO reduction with CH_4. (○,●) NO+CH_4+O_2 reaction: NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%. (□) CH_4+O_2 reaction: CH_4, 1000 ppm; O_2, 10%. Total flow rate: 100 cm^3 min^{-1}; catalyst weight: 0.1 g.

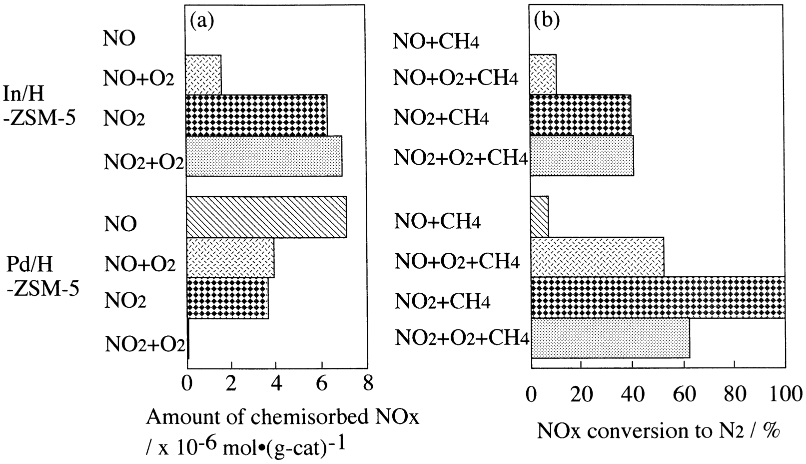


Fig. 2. NO_x chemisorption (a) and NO_x reduction with CH_4 (b) on In/H-ZSM-5 and Pd/H-ZSM-5. (a) NO_x, 100 ppm; O_2, 0 or 10%. (b) NO_x, 100 ppm; CH_4, 1000 ppm (In); 2000 ppm (Pd); O_2, 0 or 10%; H_2O, 10%. Total flow rate, 100 cm^3 min^{-1}; reaction temperature, 400°C; catalyst weight, 0.1 g (0.25 g in NO_x reduction on Pd/H-ZSM-5).

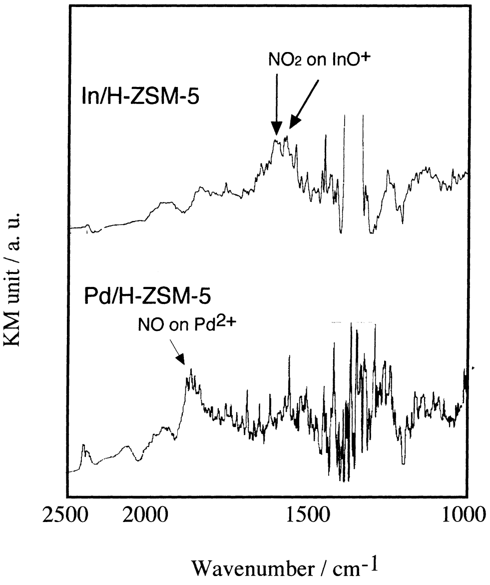


Fig. 3. Infrared spectra of NO_x adspecies under the reaction conditions of NO reduction on In/H-ZSM-5 and Pd/H-ZSM-5. NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow rate, 100 cm^3 min^{-1}; reaction temperature, 350°C.

ZSM-5, and this adspecies might be involved in the rate-determining step.

The role of NO_2 in the reaction mechanism on these catalysts must be investigated. Fig. 4 shows the dependence of initial NO_2 partial pressure on the formation rate of N_2 over In/H-ZSM-5 and Pd/H-ZSM-5 catalysts. Reaction was conducted by changing the flow rate of NO_2 and NO, totally adjusting the NO_x concentration at 1000 ppm. On In/H-ZSM-5, the N_2 formation rate increased with increasing the NO_2 partial pressure. This result also indicates that NO_2 has an important role in the reaction mechanism on In/H-ZSM-5. However, there is a maximum in the formation rate of N_2 at a ratio of $NO_2/NO_x=1/2$. It can be speculated that NO is the one more molecule of NO_x, which is needed to form N_2 more rapidly. On the other hand, the formation rate of N_2 on Pd/H-ZSM-5 increased with increasing NO_2 partial pressure used in this study. When the difficulty of NO_2 diffusion into the zeolite pore structure is considered [12], it can be deduced that the reaction NO_2–CH_4 might occur on Pd sites on the outer surface or near the pore mouth of zeolite, and that zeolite pore structure is not always needed for Pd sites.

Fig. 5 shows the catalytic activity of Pd/SiO_2 for NO_2–CH_4 reaction, as well as Pd/H-ZSM-5, as a function of O_2 concentration. It is noteworthy that Pd/SiO_2 catalyzed NO_2–CH_4 reaction as high conversion as Pd/H-ZSM-5 in the absence of O_2. The NO_2 conversion on Pd/SiO_2, however, decreased with increasing O_2 concentration, while the reaction moderately proceeded on Pd/H-ZSM-5 even at high concentrations of O_2. It is because CH_4 combustion occurs significantly on Pd/SiO_2, as shown in the figure of CH_4

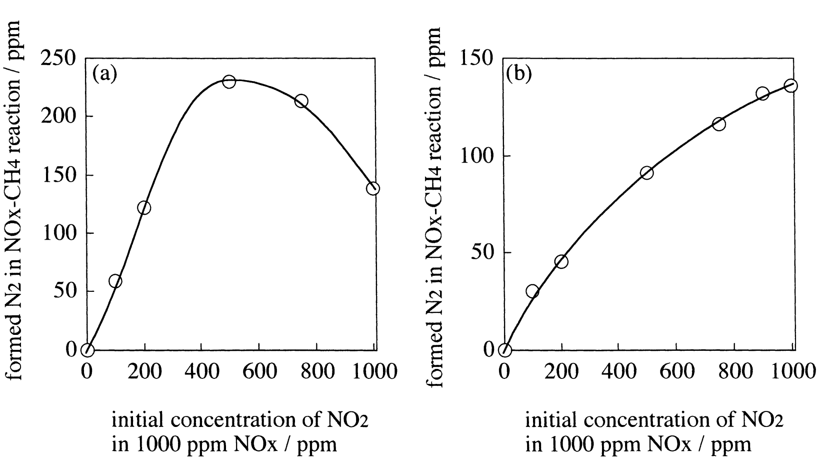


Fig. 4. Catalytic activities of In/H-ZSM-5 (a) and Pd/H-ZSM-5 (b) for NO_x reduction with CH_4 as a function of initial NO_2 concentration in the reactant feed. $NO+NO_2$, 1000 ppm; CH_4, 1000 ppm; total flow rate, 100 cm^3 min^{-1}; catalyst weight, 0.02 g (In); 0.1 g (Pd); reaction temperature, 400°C.

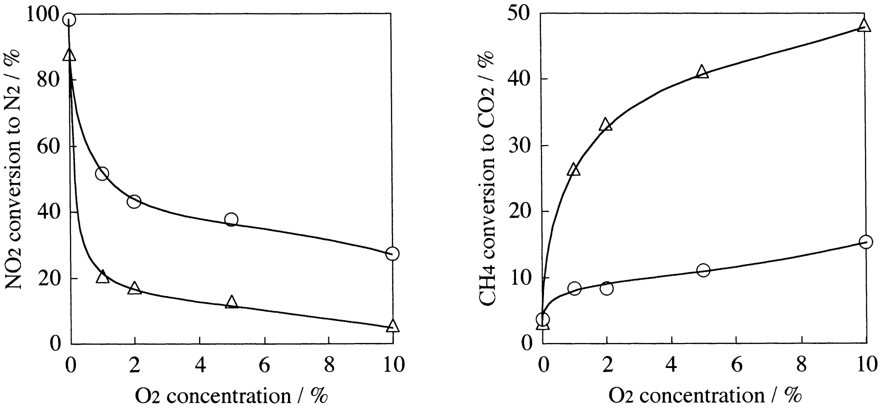


Fig. 5. Catalytic activities of Pd/H-ZSM-5 (○) and Pd/SiO_2 (△) for NO_2 reduction with CH_4. NO_2, 100 ppm; CH_4, 2000 ppm; total flow rate, 100 cm^3 min^{-1}; catalyst weight, 0.1 g; reaction temperature, 400°C.

conversion to CO_2. These results indicate that Pd locates on SiO_2 in a quite different state, compared with Pd on H-ZSM-5, although NO_2–CH_4 reaction identically occurred on both catalysts.

Fig. 6 shows the XPS spectra of Pd 3d on Pd/H-ZSM-5 and Pd/SiO_2, after the ex situ calcination at 500°C, which is the same pretreatment prior to the reaction. No intense peak attributed to Pd species was observed on Pd/H-ZSM-5, while sharp ones on Pd/SiO_2. According to the literature [20], these peaks obtained on Pd/SiO_2 were assigned to Pd oxide (PdO) species. It is easily deduced that this PdO on SiO_2 catalyzes CH_4 combustion during NO_2–CH_4 reaction in the presence of O_2, while PdO is hardly observed on Pd/H-ZSM-5. From these results, it can be concluded that the role of zeolite on the catalytic activity of Pd/H-ZSM-5 might not be due to the effectiveness of pore structures for the concentration of NO_2 adspecies, such as In/H-ZSM-5, but due to the ability of ion exchange and cation loading, resulting in high dispersion of Pd species on the zeolite structure, which is important for selective NO reduction.

As a result of this work, the reaction stage of In/H-ZSM-5 and Pd/H-ZSM-5 for NO reduction with CH_4

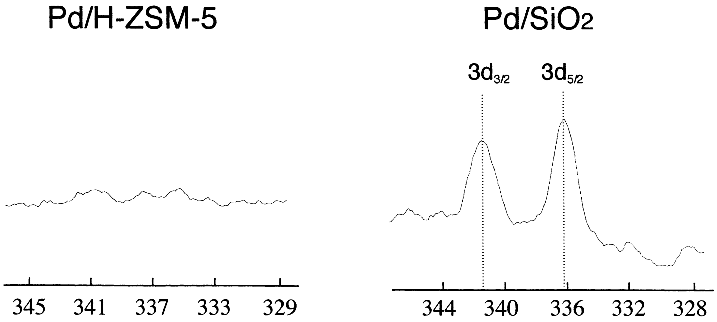
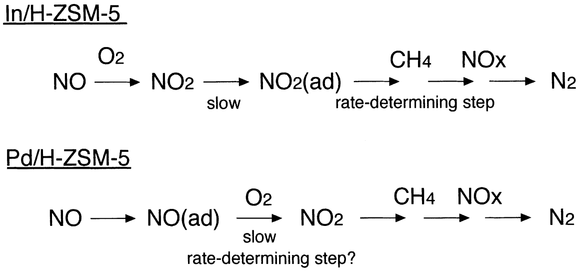


Fig. 6. XPS spectra of Pd 3d on Pd/H-ZSM-5 and Pd/SiO_2.



Scheme 1. Reaction stages in NO reduction with CH_4 on In/H-ZSM-5 and Pd/H-ZSM-5 catalysts.

can be proposed as shown in Scheme 1. The slow stages in the reaction is NO_2 chemisorption (NO_2 diffusion) on InO^+ sites inside the zeolite pore structure and the reaction between chemisorbed NO_2 and CH_4 on In/H-ZSM-5, while NO_2 formation from adspecies NO on Pd/H-ZSM-5.

4. Conclusions

Catalytic performances of In/H-ZSM-5 and Pd/H-ZSM-5 for NO reduction with CH_4 were investigated in the viewpoint of NO_2 intermediate and NO_x chemisorbed species under the reaction conditions used. NO_2 is an important species for both catalysts: the amount of chemisorbed NO_2 is proportional to the NO_x reduction activity on In/H-ZSM-5, and the catalytic activity of NO_2–CH_4 reaction on Pd/H-ZSM-5 increased with increasing partial pressure of NO_2. However, NO on Pd site was observed under the reaction conditions, and the larger amount of NO was chemisorbed on Pd/H-ZSM-5 than that of NO_2. Pd/SiO_2 showed comparable catalytic activity for NO_2–CH_4 as Pd/H-ZSM-5 in the absence of O_2, while CH_4 combustion significantly occurred because the state of Pd is in PdO on SiO_2. The role of zeolite on the catalytic activity for NO reduction with CH_4 is different between In/H-ZSM-5 and Pd/H-ZSM-5: zeolite pore structure is effective for In/H-ZSM-5 in order to concentrate NO_2 adspecies on InO^+ sites, which is involved in the rate-determining step; while zeolitic property of Pd sites located in a highly dispersed state is needed for Pd/H-ZSM-5.

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