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Stability of Pd(II) ion in side pockets of mordenite under hydrothermal conditions

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Abstract

Through the examination of stability of exchanged Pd^{2+} ion in mordenite under hydrothermal conditions by means of in situ UV–visible spectrometer, it was elucidated that Pd^{2+} ions sited in side pockets are more stable than those in main channels of mordenite.

Keywords: Mordenite; Ion-exchange site; In situ UV–visible spectrometer; Hydrothermal conditions

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1. Introduction

Ion-exchanged zeolites often show unique catalytic performance because of high dispersion of active species, low coordination number around the exchanged ions, specific valence control of the ions, and so on. Among them, Pd-zeolite is known to be active for the selective catalytic reduction (SCR) of NO_x by methane as a reductant [1–11]. Although the initial activity of Pd-zeolite on the SCR by methane is very high, gradual decrease in NO_x conversion in the presence of water vapor is a serious problem. This is due to a rapid decrease in Pd dispersion under hydrothermal conditions by agglomeration of Pd ions into PdO particles [4–10], which is a common problem of the use of ion-exchanged zeolites. As for the suppression of the agglomeration, it is known that acid sites of zeolites play essential role in the high dispersion of Pd: Pd-mordenite (MOR) shows higher stability than Pd-MFI under the SCR conditions in the presence of water vapor because of high aluminum content which results in the stable Pd^{2+} associated with an aluminum site pair [5,8,9]. In addition to the effect of acid sites, crystallographic factors of zeolites, such as channel length and distribution of framework aluminum, should significantly affect on the stability of exchanged Pd ions, however, little is examined about the effects of these factors so far. In the present study, the controlling factor of stability of Pd ions in mordenite channels under hydrothermal conditions was investigated by using in situ UV–visible spectrophotometer. To examine crystallographic factors, three types of H-mordenites, having different aluminum distribution and channel length but close chemical composition and acid strength, were used as mother zeolites.

2. Experimental

Three types of mordenites, abbreviated as SMOR, LMOR, and FMOR, were synthesized hydrothermally. SMOR and LMOR were synthesized by a conventional

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method. FMOR was synthesized by the following procedure reported previously [12]. $AlCl_3 \cdot 6H_2O$ (98%, Kanto Chemical) was dissolved in deionized water, and NaOH (99%, Tosoh Corp.) was added to precipitate, NaF (98%, Kishida Chemical) was added to the suspension, and amorphous silica produced by a wet process (Nipsil VN-3, Nippon Silica Industrial Co., Ltd.) was then added to the suspension. After stirring the reactant mixture with a spatula for ≈10 min, the mixture was transferred into a stainless steel autoclave with a volume of 80 ml and heated at 438–453 K for 72 h under an autogenous pressure while rotating at 50 rpm. After the hydrothermal treatment, the crystallized material was filtered and completely washed with boiled water for complete removal of fluorine contaminant. They were at first converted to NH_4^+-form in an aqueous solution of NH_4NO_3 at 353 K for 24 h under continuous stirring and this exchange process was performed for three times. They were converted to H-form by calcination at 773 K for 5 h in air. H-mordenite thus obtained was then ion-exchanged in an aqueous solution of $Pd(NO_2)_2(NH_3)_2$ at 353 K for 24 h, followed by filtration, dryness at 383 K for 24 h, and calcination at 773 K for 5 h in air. In situ UV–visible spectra were measured by a JASCO V-570 spectrophotometer equipped with a VHR-630 vacuum heating reflection unit [13]. After the 50 mg of Pd-mordenite was heated at 773 K in flowing 7% O_2/He for 1 h, the spectra were measured at 673 K in flowing 2% H_2O/He at a flow rate of 100 $ml\,min^{-1}$. FT/IR spectra of adsorbed acetonitrile were recorded with a JASCO FT/IR-300 equipped with an in situ quartz cell connected to a vacuum system. The self-supporting disk was evacuated at 673 K for 1h, calcined in 13.3 kPa of O_2 for 1 h, and cooled to room temperature. Then the sample disk was exposed to 1.3 kPa of CH_3CN for 1 h, followed by evacuation at room temperature for 1 h. SEM images were obtained by a HITACHI S-800S. NH_3-temperature programmed desorption (NH_3-TPD) profiles were measured with a Bel Japan Multitask TPD apparatus equipped with a quadlepole mass spectrometer. Pd K-edge XANES spectra were obtained at the BL-10B of the Photon Factory in the National Laboratory for High Energy Physics, working at 2.5 GeV with a current at 175–185 mA [14]. The samples exposed to O_2/He or H_2O/He at 773 K were rapidly cooled to room temperature in a flow of He and were sealed in XAFS cells having Kapton windows without exposure to air. The Fourier Transforms of k^3-weighted Pd K-edge EXAFS was obtained in the range of Δk: 4–15 $Å^{-1}$.

3. Results and discussions

As shown in Table 1, the size and morphology of mordenite crystal were significantly different. SMOR was composed of hexagonal plate-like crystals, in which diameter of basal plane was 0.2–0.4 μm and the length along *c*-axis was 0.06–0.1 μm. LMOR showed about 10 times larger size in both *c*-axis and basal plane. On the other hand, FMOR crystals showed rod-like morphology, having 0.7–0.8 μm in *c*-axis length and 0.08–0.1 μm in basal plane diameter. Since mordenite has main channels that run along the c-axis [15], a difference of the c-axis length is equivalent to that of intracrystalline diffusion pathway. Si/Al ratio and Pd ion-exchange level were almost the same among all of the samples examined. From a comparison of NH_3-TPD profiles, it was confirmed that the acid strength and the acid amount of these H-form mordenites were almost the same. The profiles were composed of a desorption peak at lower temperatures (L-peak) due to a weakly held ammonia and a peak at higher temperatures (H-peak) ascribed to the strong acid sites [16]. For all the H-form mordenites, the H-peak started from 473 K, showing the peak maximum at 682 K, and terminated at 873 K. The acid amounts determined from the H-peaks were the same within an experimental error, i.e., 1.26 $mmol\,g^{-1}$ for H-SMOR, 1.23 $mmol\,g^{-1}$ for H-LMOR, and 1.23 $mmol\,g^{-1}$ for H-FMOR, respectively.

Table 1
Profile of Pd-exchanged mordenites

Sample	Lc* (μm)	Si/Al ratio	Pd content (wt.%)	Ion-exchange level (%)
Pd-SMOR	0.06–0.1	7.9	0.86	10.1
Pd-LMOR	0.5–1.5	8.5	0.79	10.8
Pd-FMOR	0.7–0.8	7.6	0.81	10.9

* Crystal size along *c*-axis determined from SEM images.

Fig. 1 shows IR spectrum of adsorbed acetonitrile on H-form mordenites at room temperature in the *ν* (CN) vibration region. As for the H-SMOR and H-LMOR, the absorption bands assignable to CN stretching were observed at 2280, 2305, 2317 and 2335 cm^{-1}. According to the assignment by Marie et al. [17], the former three bands are assigned to adsorbed acetonitrile interacting with OH groups, and the small band at 2335 cm^{-1} is assigned to acetonitrile coordinated to Lewis acid sites. The relative intensities of the band at 2335 cm^{-1} are almost the same, indicating there is not a significant difference in extra-framework aluminum and/or Lewis acid sites on framework Al. The splitting of the bands at 2305 and 2317 cm^{-1} can be assigned to the difference in the adsorption site of acetonitrile in the mordenite channels, i.e., the band at 2305 cm^{-1} is attributed to *ν*(CN) frequency of acetonitrile adsorbed on OH groups in main channels, while the band at 2317 cm^{-1} is those in side pockets of mordenite. Actually, in the higher wavenumber region, two negative *ν*(OH) bands at 3620 cm^{-1} and 3600 cm^{-1} were observed by the adsorption of acetonitrile, indicating the perturbation of free