

Xenon probe for detecting the microporous structure of nanosized HZSM-5 zeolite

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The secondary pores in the nanosized HZSM-5 zeolite have been observed for the first time via ^{129}Xe NMR spectroscopy using xenon as a probe; the location of non-framework Al can also be identified.

As an emerging member of nanometer materials, nanosized zeolites have received considerable attention in the field of catalysis owing to their unique properties. When the crystallite size of HZSM-5 zeolite is reduced to the nanoscale level, it exhibits higher catalytic activity, less coking and longer catalytic life in the conversion of methanol to hydrocarbons,¹ oligomerization of ethylene, *etc.*² At present, there is growing interest in the synthesis of nanosized zeolites.^{3,4} However, few attempts have been made to characterize the microporous structure of nanosized zeolites. In particular, the effects of crystallite size down to the nanoscale level on the microporous structure of zeolites have not been well established in the literature. ^{129}Xe NMR spectroscopy is a powerful technique for investigating porous materials, especially zeolites.^{5–7} The high polarizability of the xenon electron cloud makes it very sensitive to physical interactions with its environment. Here we use xenon as a probe molecule for detecting the variations of microporous structure of dealuminated HZSM-5 zeolites with crystallite sizes of < 100 nm.

The starting HZSM-5 samples (Si/Al = 28) with crystallite sizes of 1000 and 70 nm were prepared according to the procedure published in our previous papers.^{8–10} Hydrothermal treatment was performed in a quartz reactor tube with 10 mm maximum bed depth of zeolite. The temperature was increased at a rate of 5 °C min⁻¹ to the treatment temperatures of 400 and 700 °C, then 100% water vapor (0.1 MPa) was introduced for 2 h. As established by ^{27}Al MAS and ^1H – ^{27}Al CP/MAS NMR spectra, there is little non-framework Al in the parent micro-sized and nanosized HZSM-5 zeolites.¹⁰ However, hydrothermal treatment of the samples leads to dealumination of the zeolite frameworks and to gradual formation of non-framework Al (δ_{Al} at 0 and 30 ppm).¹¹

Prior to adsorption, all samples were degassed typically at 723 K and a pressure below 10⁻² Pa for 10–20 h. ^{129}Xe NMR spectra were collected at room temperature on a Bruker DRX-400 spectrometer operating at 110.6 MHz with a recycle delay of 1 s, 60° pulse width of 8 μs and 1000–4000 scans. Chemical shifts were referenced to a secondary standard of xenon adsorbed in NaY zeolite the resonance of which was previously referenced to xenon gas at zero pressure using Jameson's equation.¹²

XPS measurements were carried out in a modified Leybold LHS-12 MCD system using Mg-K α excitation and pass energy of 100 eV. The Si/Al ratio on the external surface of the zeolites can be obtained by integrating the calibrated Si 2p (E_{b} = 102.9 eV) and Al 2p (E_{b} = 74.3 eV) peaks.

The ^{129}Xe NMR spectra of parent micro-sized and nanosized HZSM-5 zeolites are shown in Fig. 1. With increase of xenon uptake, the resonance positions shift to low field due to the predominance of Xe–Xe interactions with an increase of xenon

concentration. One main signal with a weak high-field shoulder is observed in the spectra of parent micro-sized HZSM-5 [Fig. 1(a)]. The main peak is associated with xenon adsorbed in the internal channels of micro-sized HZSM-5. However, for the nanosized HZSM-5, with increase of xenon uptake, a new strong peak appears at higher field [Fig. 1(b)]. The intensity of this new peak increases with xenon pressure up to 400 Torr. Further increase of xenon concentration, however, results in a decrease of the peak intensity where it is observed as a shoulder peak of the low-field signal. It is well known that the average electrostatic field in the internal channels of HZSM-5 zeolite is much stronger than that on the external surface.⁶ Thus, xenon is adsorbed preferentially in the internal channels, and its chemical shift is at the low field. When the crystallite size of HZSM-5 zeolite is reduced to the nanoscale level, as demonstrated by a transmission electron microscope (TEM),⁸ the particles are present as aggregates of many nanosized crystals with void space between the crystallites, for a high surface energy. Nanosized HZSM-5 zeolite has many secondary pores, which differ from the internal channels. With increasing xenon uptake, more xenon will be distributed in the secondary pores of nanosized HZSM-5, of this, some is adsorbed on the external surface of nanosized HZSM-5 whilst the remainder occupies the void space of the secondary pores. Therefore, as shown in Fig. 1(b), two signals are observed in the ^{129}Xe NMR spectra of nanosized HZSM-5. The low-field peak is assigned to xenon in the internal channels of nanosized zeolite, while the high-field peak is attributed to xenon in the secondary pores. However, under conditions of less aggregation,⁸ the xenon signal of the secondary pores appears as a weak shoulder in the spectra of micro-sized HZSM-5 [Fig. 1(a)]. In addition, it can also be seen from Fig. 1(b) that the line width of the high-field peak is much narrower than that of the low-field peak. This may be due to a higher mobility of xenon atoms in such sites caused by weaker interaction among xenon atoms, which implies that the secondary pore size of the nanosized zeolite might be greater than that of its internal channels.

If we plot the resonance positions of xenon in the internal channels and in the secondary pores of nanosized HZSM-5 at

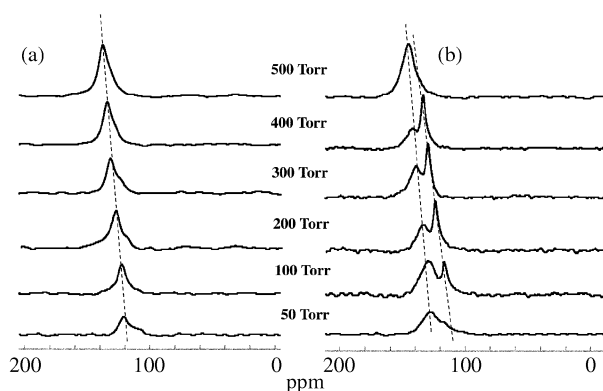


Fig. 1 ^{129}Xe NMR spectra of xenon adsorbed in parent micro-sized (a) and nanosized (b) HZSM-5 zeolites as a function of xenon pressure.

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different pressures [Fig. 1(b)], it is found that the slopes of these two lines are different and at higher xenon pressures these two lines will be superposed. This indicates that the chemical shift difference between xenon in the internal channels and in the secondary pores decreases slightly with pressure. Xenon atoms in these two positions also exchange at room temperature and when the xenon pressure is > 500 Torr, this exchange is too fast to be detected by NMR. Thus, one main signal is observed in the ^{129}Xe NMR spectra of nanosized HZSM-5 at higher xenon pressures. To our knowledge, this is the first report that secondary pores in nanosized zeolites are observed by ^{129}Xe NMR spectroscopy.

Fig. 2 and 3 show the ^{129}Xe NMR spectra of microsized and nanosized HZSM-5 zeolites treated by steaming at 400 and 700 °C. There is only a single signal in the ^{129}Xe NMR spectra of microsized HZSM-5 dealuminated by steaming (Fig. 2). This demonstrates that the non-framework Al may migrate to the external surface of the dealuminated microsized HZSM-5, in the presence of steam, leading to a homogeneous distribution of xenon in the channels. However, two signals are evident in the ^{129}Xe NMR spectra of nanosized HZSM-5 treated by steaming at 400 °C [Fig. 3(a)]. The obvious distribution of xenon in the

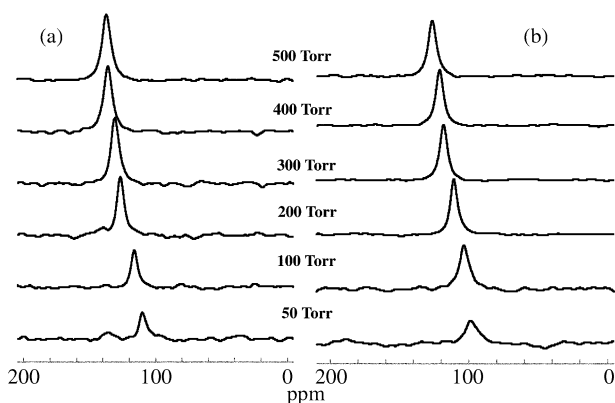


Fig. 2 ^{129}Xe NMR spectra of xenon adsorbed in dealuminated microsized HZSM-5 zeolite steamed at 400 °C (a) and 700 °C (b) as a function of xenon pressure.

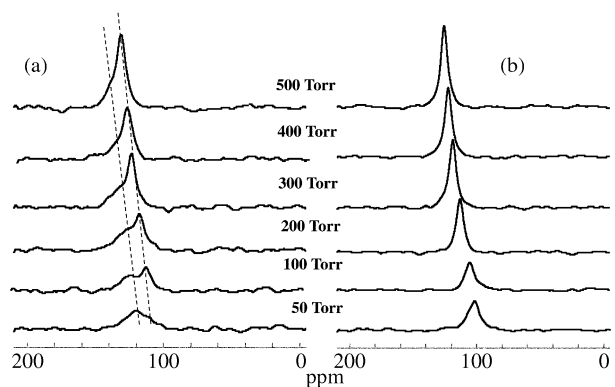


Fig. 3 ^{129}Xe NMR spectra of xenon adsorbed in dealuminated nanosized HZSM-5 zeolite steamed at 400 °C (a) and 700 °C (b) as a function of xenon pressure.

secondary pores of nanosized HZSM-5 indicates that most non-framework Al does not deposit on the external surface of the nanocrystallites. The two lines from the resonance positions of xenon adsorbed in the internal channels and in the secondary pores will not be superposed at high xenon pressures [Fig. 3(a)]. This indicates that the existence of non-framework Al hinders the rapid exchange of the xenon atoms in these two positions. One can speculate that the non-framework Al may deposit near the windows of the nanosized HZSM-5 channels. If hydrothermally treated at higher temperatures, such as at 700 °C, only one signal appears in the ^{129}Xe NMR spectra [Fig. 3(b)]. Thus, the non-framework Al may occupy the secondary pores of nanosized HZSM-5 (*i.e.* on the external surface).

XPS experiments were performed to study the migration of Al atoms in zeolites. It was found that the Si/Al ratio on the external surface of microsized HZSM-5 decreases from 12.5 to 3.5 after steaming at 700 °C, while that of nanosized HZSM-5 decreases from 6.3 to 3.2 under the same conditions. Therefore, hydrothermal treatment of both microsized and nanosized HZSM-5 will lead to Al enrichment on the external surface *i.e.* migration of Al atoms to the external surface. A similar result was obtained by Datka *et al.*¹³ in characterizing a dealuminated HZSM-5 zeolite. This also agrees well with the above results from ^{129}Xe NMR.

In conclusion, xenon is a sensitive probe to detect zeolite microporous structure and its variation upon dealumination. Evidence of secondary pores are observed for the first time in the ^{129}Xe NMR spectra of nanosized HZSM-5 zeolite. After hydrothermal treatment, the location of non-framework Al can also be determined.

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