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High resolution adsorption isotherms of N_2 and Ar for nonporous silicas and MFI zeolites

Kazuyuki Nakai · Joji Sonoda · Masayuki Yoshida · Masako Hakuman · Hiromitsu Naono

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Abstract The high resolution adsorption isotherms of N_2 (77.4 K) and Ar (87.3 K) have been measured for two nonporous silicas with different silanol contents (3.3 and 0.35 OH/nm^2) and for two MFI zeolite with different Al contents (Si/Al = 12.5 and 500). Silanol groups and Al sites (acid sites) gives the significant effect on the N_2 isotherms at submonolayer, but the Ar isotherms are independent of silanols and Al sites. The Ar isotherms, therefore, are preferable in calculation of microporosity of zeolites. The N_2 and Ar isotherms for MFI zeolite (Si/Al = 500) have been measured at temperatures of 77–94 K, from which the differential adsorption energies of N_2 and Ar are calculated. The interaction of N_2 with channel surface of MFI zeolite is greater than that of Ar in the range of $\alpha_s = 0.1$–0.7. The hystereses are detected for the N_2 isotherm in $p/p^o = 0.1$–0.3 at 77.4 K and for the Ar isotherm in $p/p^o = 3 \times 10^{-4}$–2×10^{-3} at 87.3 K. However, it is difficult to explain the hysteresis phenomenon using differential adsorption energy.

Keywords MFI zeolite · ZSM-5 · Silicalite · Adsorption isotherms of N_2 and Ar · Differential adsorption energy

1 Introduction

Recent progress of the adsorption apparatus makes it possible to measure the N_2 and Ar adsorption isotherms from $p/p^o = 10^{-8}$ to $p/p^o = 0.998$ (Nakai et al. 2006a, 2006b). Accordingly, it is able to evaluate the adsorption behavior of these adsorbates in detail from submonolayer to multilayer; namely, $\alpha_s = 0.01$–8. The present work consists of the two parts; one is to examine effect of silanol groups of silica or acid sites of MFI zeolites on the high resolution adsorption isotherms of N_2 and Ar at their boiling points, and the other is to investigate the differential adsorption energy of N_2 and Ar with the micropore channels of MFI zeolite from micropore filling as low as $\alpha_s = 0.1$. In the present work, we will show that the high resolution isotherms of N_2 and Ar give an important information about characterization of silica surface and channel surface of microporous MFI zeolite.

K. Nakai (✉) · J. Sonoda · M. Yoshida · M. Hakuman · H. Naono
BEL-Japan, INC, Haradanaka, Toyonaka-shi, Osaka, 561-0807, Japan
e-mail: kazu@nippon-bel.co.jp

2 Experimental

Two kinds of the nonporous silicas were used in this work. The hydroxylated silica was prepared by immersing fine silica particles (Aerosil-200) in distilled water, while the dehydroxylated silica was prepared by heating hydroxylated silica at 1000 °C for 4 h in vacuo. Prior to the N_2 or Ar adsorption, the silica samples were pretreated at 110 °C for 4 h in vacuo. The silanol contents of the two silicas were evaluated from the BET monolayer value of the water isotherm at 25 °C (Naono et al. 2000). Two samples of MFI zeolites ($SiO_2/Al_2O_3 = 1000$, $SiO_2/Al_2O_3 = 25$) were the reference materials of Catalysis Society of Japan (JRC-Z5-1000H, JRC-Z5-25H). MTW (ZSM-12) was kindly supplied from Y. Kubota of Yokohama National University. Prior to gas adsorption measurement, the zeolite samples were pretreated in vacuo at 350 °C for 10 h.

The high resolution adsorption isotherms of N_2 at 77.4 K (boiling point of liquid nitrogen) and Ar at 87.3 K (boiling point of liquid argon) were measured by BELSORP-max, which has three pressure transducers of 0.0133 kPa, 1.33 kPa and 133 kPa in full scale. Using these transducers,

it is possible to measure the adsorption isotherm of N_2 or Ar from $p/p^o = 10^{-9}$ to saturation pressure. The Ar isotherm at 94 K was measured by the volumetric adsorption apparatus (BELCryo), in which the cryostat is incorporated.

The N_2 and Ar isotherms measured by BELSORP-max are changed into the α_s-curve, where α_s is defined as $V_a/V_{0.4}$ (V_a: adsorbed amount at arbitrary pressure, and $V_{0.4}$: adsorbed amount at $p/p^o = 0.4$).

3 Results and discussion

3.1 High resolution adsorption isotherms of N_2 and Ar for nonporous silicas and microporous MFI zeolites at their boiling points

Figures 1a and 1b show the high resolution adsorption isotherms of N_2 (77.4 K) and Ar (87.3 K) for the hydroxylated silica ($A_{BET} = 188$ m^2/g) and the dehydroxylated silica ($A_{BET} = 168$ m^2/g) whose silanol content was evaluated to be 3.3 OH/nm^2 and 0.35 OH/nm^2, respectively. The results shown in Figs. 1a and 1b clearly indicate that the N_2 isotherms at the submonolayer range ($\alpha_s = 0.01$–0.5) have different patterns for the two silicas, while the two Ar isotherms almost overlap one another below $\alpha_s = 1.0$. It is evident that the surface silanol groups give a significant effect on the N_2 isotherms below $\alpha_s = 0.5$, but the silanols give little influence on the Ar isotherms.

Figures 2a and 2b show the high resolution adsorption isotherms of N_2 (77.4 K) and Ar (87.3 K) for the two kinds of microporous MFI zeolites in which the ratio of Si/Al is 12.5 and 500, respectively. At the submonolayer coverage ($\alpha_s = 0.01$–0.6), the two Ar isotherms almost overlap one another (cf. Fig. 2b), but there is remarkable difference in the two N_2 isotherms below $\alpha_s = 0.25$ (cf. Fig. 2a). It is shown that the MFI sample having a large Al content (Si/Al = 12.5) gives large effect for the N_2 isotherms; in other words, the Al sites (i.e., acid sites) in MFI zeolite give a significant influence on the N_2 adsorption isotherms.

The experimental facts found in the silica samples and in the MFI samples are closely correlated with the molecular characters of N_2 and Ar. It is well-known that the N_2 molecule is specific adsorptive having quadrupole moment, while Ar atom is nonspecific adsorptive where van der Waals force is the main factor in the Ar adsorption (Gregg and Sing 1982). The present adsorption data given in Figs. 1 and 2 in-

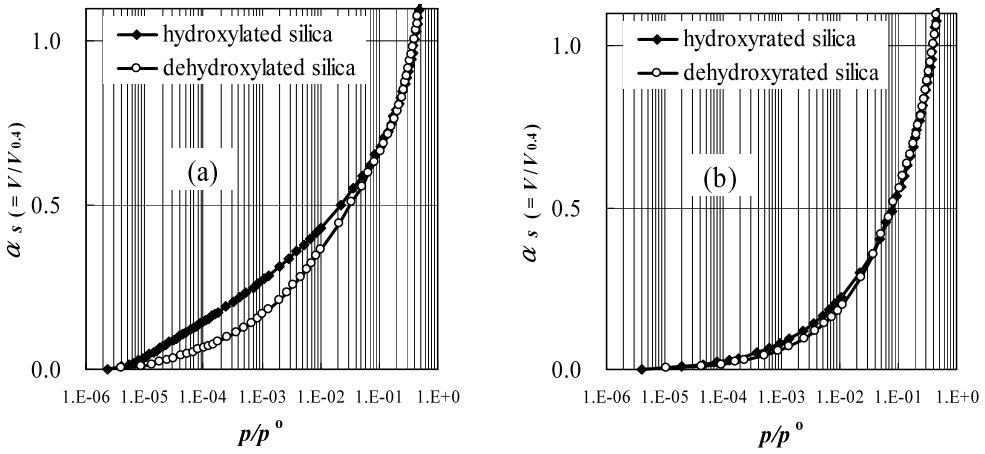

Fig. 1 High resolution adsorption isotherms for nonporous silicas; (**a**) N_2 isotherms at 77.4 K (**b**) Ar isotherms at 87.3 K

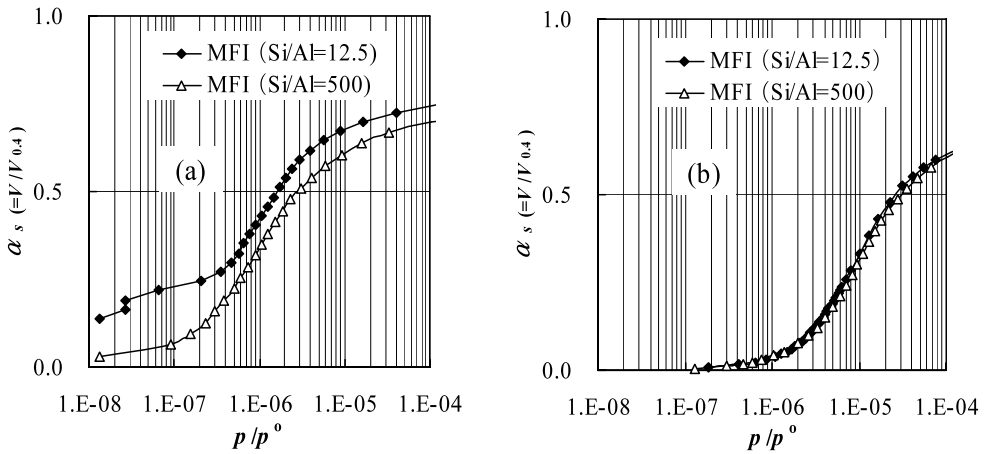

Fig. 2 High resolution adsorption isotherms for MFI zeolites; (**a**) N_2 isotherms at 77.4 K (**b**) Ar isotherms at 87.3 K

dicate that the interaction of the quadrupole moment of nitrogen molecule with the silanol group on the nonporous silica surface or with the Al-sites (acid sites) present in the microporous channels of MFI zeolites can be detected in their adsorption isotherms in the submonolayer range.

The high resolution Ar isotherms are preferable for calculation of microporosity of zeolites, because the Ar adsorption isotherms from $p/p^o = 10^{-7}$ to $p/p^o = 10^{-4}$ are independent of the Al content of zeolites. In Fig. 3, the pore size distribution of the two MFI zeolites having Si/Al = 12.5 and Si/Al = 500 were calculated by the Grand Canonical Monte Carlo simulation method (BELSim) developed by BEL JAPAN, Inc., where the Ar isotherms given in Fig. 2b were used. The two zeolites [MFI (Si/Al = 12.5) and MFI (Si/Al = 500)] give the same peak position of $d_p = 0.56$ nm, whose pore size corresponds to the channel size of MFI zeolite shown in Fig. 4. The minute peak near $d_p = 1$ nm, which arises from the step of the Ar isotherm in the vicinity of $p/p^o = 10^{-3}$ (cf. Fig. 5a). Similar calculation was carried out using the N_2 isotherm (cf. Fig. 5a). The main peak appears at $d_p = 0.56$ nm, but the second small peak is detected at $d_p = 10$ nm, whose peak is due to the step in N_2 isotherm (ca. $p/p^o = 0.1$) (cf. Fig. 5a). Accordingly, it is reasonable to conclude that the main peak at $d_p = 0.56$ nm is due to MFI channel pores, and the second peaks at $d_p = 1$ or 10 nm is not related to the pores of MFI channels, but to the ghost peak.

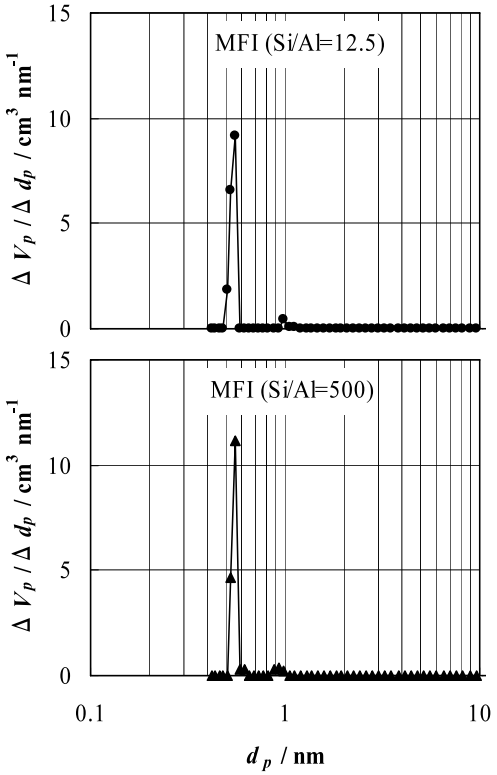

Fig. 3 Pore size distributions for MFI zeolites (GCMC, BELSim)

3.2 Comparison of high resolution isotherms of N_2 and Ar for microporous MFI zeolite (Si/Al = 500)

It is significant to compare the high resolution isotherms of N_2 and Ar for MFI zeolite, because, as was pointed before, N_2 is specific adsorptive and Ar nonspecific one. Figure 5a show the high resolution adsorption isotherms of N_2 and Ar in the range of $\alpha_s = 0.01$–1.1 for the MFI zeolite (Si/Al = 500) at their boiling points. Below $\alpha_s = 0.6$, as was seen from Fig. 5a, the N_2 isotherm is shifted to low relative pressure in comparison with the Ar isotherm, whose result suggests that interaction of N_2 with channel surface of MFI

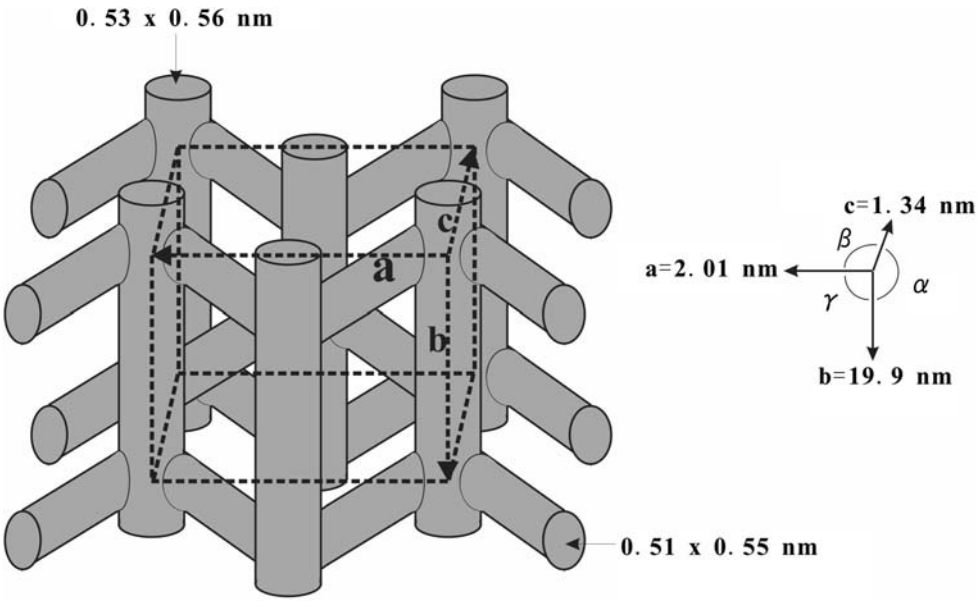

Fig. 4 Channel structure of MFI zeolites

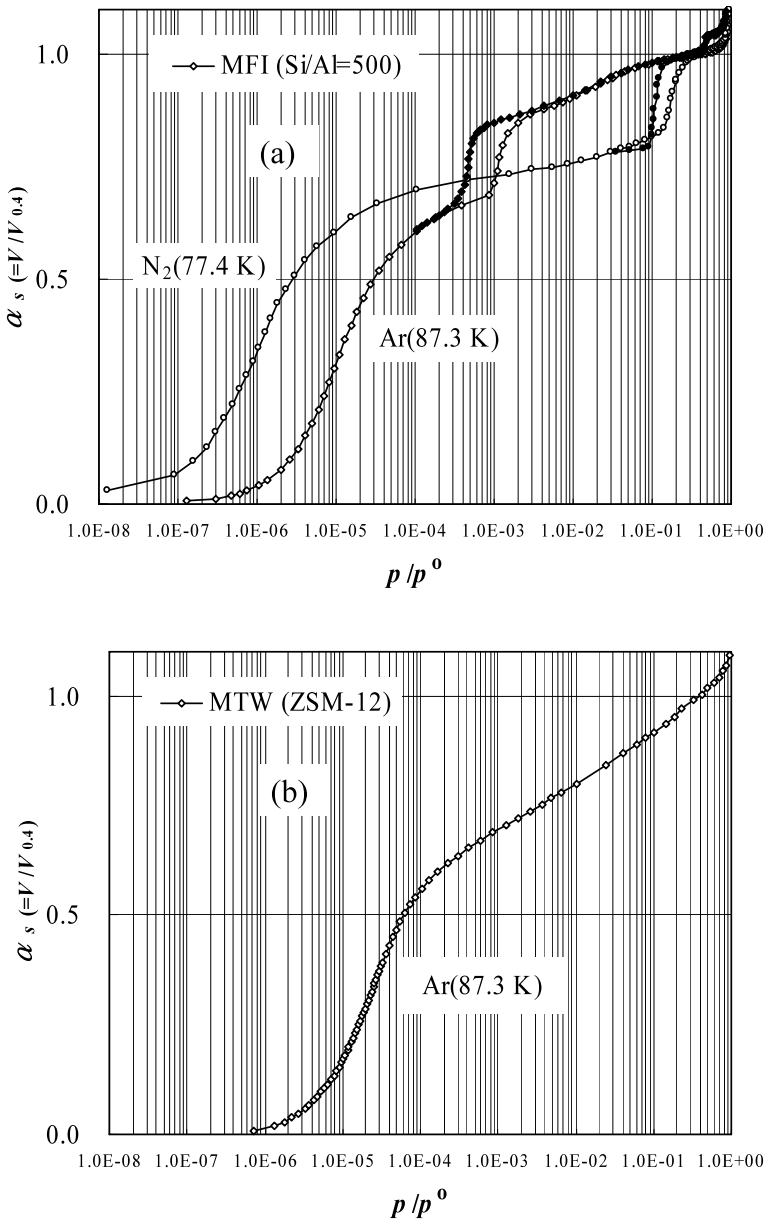

Fig. 5 High resolution adsorption isotherms for zeolites; (**a**) Ar and N_2 isotherms for MFI (**b**) Ar isotherm for MTW

zeolite (Si/Al = 500) is larger than that of Ar. Their adsorption energies will be given in the next section.

In both isotherms, the hystereses are detected; namely, the N_2 isotherm has hysteresis at $p/p^o = 0.1$–0.2, while the Ar isotherm has hysteresis at $p/p^o = 3 \times 10^{-4}$–2×10^{-3}. The hysteresis of the N_2 isotherm for the present MFI zeolite (Si content = 99.6 mole%) is almost same as that reported by Muller and Unger (1988) for silicalite (Si content: 100%). There is a large difference in the relative pressure of hysteresis between N_2 and Ar isotherms, but it is difficult to explain this difference in the present stage.

It is interesting to examine whether other zeolites give the hystereses (steps) shown in Fig. 5a. It was found that several zeolites (MTW, AFI, VFI, LTA, FAU) give no step in the high resolution Ar isotherms at 'the vicinity of $p/p^o = 10^{-3}$ (Nakai et al. 2007). For example, the Ar isotherm for the MTW zeolite (ZSM-12) is shown in Fig. 5b. We speculate that the hystereses detected in the N_2 and Ar isotherms are related to the channel structure of MFI zeolite, which consists of straight channels (channel size: 5.3 × 5.6 (Å)) and zigzag channels (channel size: 5.1 × 5.5 (Å)) (cf. Fig. 4).

3.3 Comparison of differential adsorption energy of N_2 and Ar for microporous MFI zeolite (Si/Al = 500)

In the previous section, it is suggested that interaction of N_2 molecules with channel surface of MFI zeolite (Si/Al = 500) is greater than that of Ar atoms. In this section, the differential adsorption energies of N_2 and Ar are calculated on

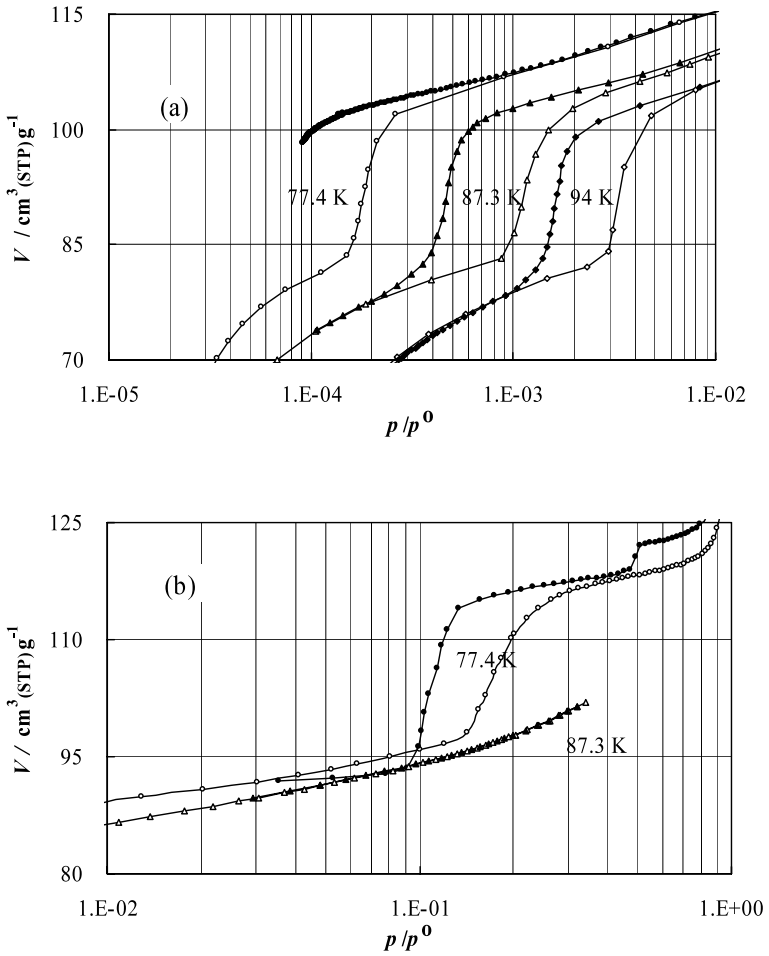

Fig. 6 High resolution adsorption-desorption isotherms for MFI zeolite (Si/Al = 500); (**a**) Ar isotherms (**b**) N_2 isotherms

the basis of the high resolution isotherms of both adsorbates. The Ar isotherms at 77.4 K, 87.3 K, and 94 K are shown in Fig. 6a, while the N_2 isotherms at 77.4 and 87.3 K are shown in Fig. 6b. In the N_2 isotherm at 77.4 K, there appear two hystereses; one above $p/p^o = 0.45$, which may be attributed to capillary condensation, and the other at $p/p^o = 0.1$–0.3, which may be attributed to the change of packing density of N_2 molecules trapped in the channel of MFI zeolite (Muller and Unger 1988). This phenomenon, however, has not been clarified yet.

In Fig. 7, the differential adsorption enthalpies ($\Delta\bar{h}_{ad}$) of N_2 and Ar are given as a function of α_s. At first, we shall consider the adsorption energy at low filling, where the lateral interaction of adsorbates trapped in microporous channels of MFI is assumed to be small. As was shown in Fig. 7, the differential adsorption energies for N_2 and Ar at $\alpha_s = 0.1$ are 10.0 kJ/mol and 5.0 kJ/mol, respectively. This experimental fact clearly indicates that the vertical interaction energy of the N_2 molecules with the channel surface of MFI zeolite is twice of that of the Ar atoms. Such difference in interaction energy may be due to the difference in character of two adsorptives; that is, N_2 is specific adsorptive with quadrupole, while Ar is nonspecific adsorptive (noble gas).

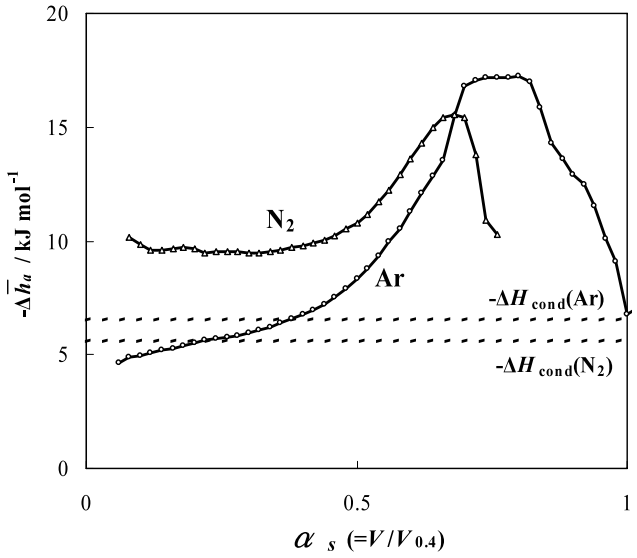

Fig. 7 Differential adsorption enthalpies for MFI zeolite (Si/Al = 500)

Next, the lateral interaction of the two adsorbates will be considered. In case of Ar (cf. Fig. 7), its differential

adsorption energy increases from 5.0 kJ/mol ($\alpha_s = 0.1$) to 17.4 kJ/mol ($\alpha_s = 0.7$), reaches maximum 17.4 kJ/mol ($\alpha_s = 0.7$–0.8), and then decreases to condensation energy 6.52 kJ/mol (87.3 K). On the other hand, in case of N_2, its differential adsorption energy increases from 10.0 kJ/mol ($\alpha_s = 0.1$) to 15.4 kJ/mol ($\alpha_s = 0.6_7$), reaches maximum 15.4 kJ/mol ($\alpha_s = 0.6_7$–0.7), and then decreases. From difference in the adsorption energies at $\alpha_s = 0.1$ and $\alpha_s = 0.7$, it is inferred that the lateral interaction of Ar atoms in the micropore channels of MFI zeolite is greater than that of N_2 molecules. This result is in sharp contrast to the vertical interaction mentioned above.

As was mentioned above, there is a large difference in hysteresis pressure between N_2 isotherm and Ar isotherm (cf. Fig. 5a). We tried to find the relation between difference in hysteresis pressure and difference in adsorption energies (vertical and lateral interactions), but it was unable to find the relation.

Finally, the phase transition of MFI zeolite crystal (ZSM-5) will be mentioned in connection with the hysteresis detected in the adsorption isotherm. It is known that the monoclinic-orthorhombic phase transition of MFI zeolites occurs at temperatures of 330–360 K, depending on Al content of MFI zeolite (Mentzen et al. 1996). Takaishi and Tsutsumi (1996) have pointed out that the hysteresis of *p*-xylene in its adsorption isotherm (352 K) is related to phase transition of ZSM-5 zeolite crystal. There is the large difference in temperature between the ZSM-5–*p*-xylene system (352 K) and the present adsorption system (77 K–94 K). It is very important to investigate whether the phase transition of MFI zeolite crystal is brought about by the adsorption of N_2 or Ar. The diffraction study of this problem is now in progress.

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