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Adsorption behavior of N_2 and Ar molecules in Type Y zeolite with different surface properties (SiO_2/Al_2O_3)

The surface areas and pore-size distributions of porous and non-porous solids are frequently inferred from nitrogen adsorption measurements. Nitrogen adsorption is the method of choice because of its sensitivity, precision, and low cost. However, in some cases, nitrogen adsorption isotherms can provide misleading estimates of pore-size distributions. In such cases, inert gases such as argon is typically used instead. In this application note, we examine the differences between the adsorption isotherms of N_2 at 77.4 K and Ar at 87.4 K in Y-type zeolites.

Molecular nitrogen, N_2, which has a quadrupole moment, is strongly adsorbed on Al cation sites in zeolites, while non-polar argon does not interact as strongly with these adsorption sites. The isotherms plotted in Fig. 2 below are shown in terms of adsorbed amount (given in units of gas volume at STP) against relative pressure. The relative pressure is the ratio of the actual measurement pressure (p) to the saturation vapor pressure (p_0) of the gas phase at the measurement temperature. As synthesized, Y-type (FAU) zeolites have high aluminum contents and low hydrothermal stability. Before these materials can be used as

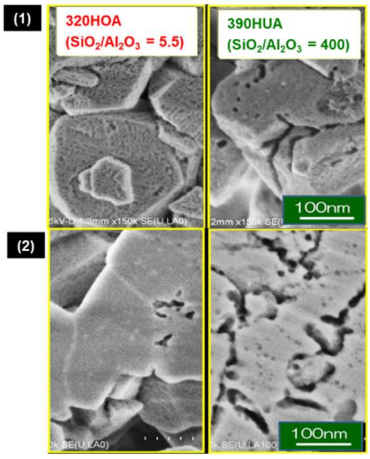

Fig. 1 FAU zeolite SEM image of diffrent SiO_2/Al_2O_3=5.5 and 400
(1) Surface image of HSZ particles / (2) Cross-sectional image

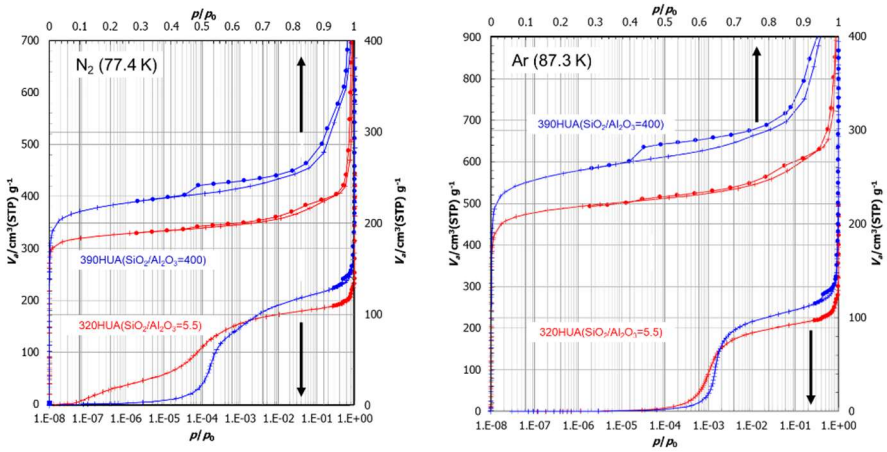

Fig 2. Adsorption isotherms of Y-type zeolite (N_2@77.4K, Ar@87.4K)

industrial catalysts, they are usually converted to ultra-stable Y (USY) zeolites with low aluminum contents by steaming at high temperature. The de-alumination process preserves the zeolites' micropore structures while increasing their Si/Al ratios and creating meso- and macropores. The FE-SEM surface images in Fig. 1(1) and the cross-sectional images after BIB (broad ion beam) treatment in Fig. 1(2) show this for samples of Y-type zeolite 320HOA (SiO_2/Al_2O_3=5.5) and its ultra-stable, de-aluminated analog 390HUA (SiO_2/Al_2O_3=400) provided by Tosoh Corp. Fig. 1 shows the adsorption isotherms of N_2 and Ar at 77.4 K and 87.3 K, respectively, on both zeolites. These isotherms were measured using the BELSORP MAX after pretreatment at 300°C for 8 hours *in vacuo*. The isotherms were

measured from extremely low relative pressures (10^{-8}) to near saturation (ambient) pressure. In the IUPAC isotherm classification scheme, both sets of adsorption isotherms are classified as Type I+IV. Type I isotherms are characteristic of purely microporous solids. In micropores (pore diameter < 2 nm), adsorbed molecules interact strongly with the atoms of the pore walls because of their close physical proximity (up to approximately two or three times the molecular diameter), resulting in the classical Langmuir isotherm shape. The low-pressure portions of the isotherms in Fig. 2 show this type of behavior. At higher pressures, the micropores are almost completely filled, and adsorbate molecules begin coating the surfaces of mesopores (2 nm < pore diameter < 50 nm) and macropores (diameter $\geq$ 50 nm). Further increases in pressure result in multilayer adsorption or condensation within the mesopores and macropores. Condensation/multilayer formation cannot occur within micropores because of spatial constraints. The isotherms in Figure 1 show both the adsorption (increasing pressure) and desorption (decreasing pressure) branches; when the adsorption and desorption branches of an isotherm do not coincide, i.e., when there is *hysteresis* in the isotherm, this indicates condensation within meso- and macropores. Attractive forces between sorbate molecules and pore walls favor the condensed phase over the gas phase. As a result, the desorption branches of the hysteresis loops in Fig. 1 are above the adsorption branches.

The lower (logarithmic scale) N_2 isotherm plots in Fig. 2 show significant differences in the N_2 loadings of the two zeolites at low relative pressures. The loading of N_2 in the smallest micropores (corresponding to the lowest pressures) of 320HUA is enhanced relative to the N_2 loading in its de-aluminated analog 390HUA because of attractive interactions between the N_2 quadrupoles and the Al^+ cation centers in 320HUA. This effect is not observed for non-polar Ar. Fig. 3 shows that N_2 is strongly adsorbed within the micropores of 320HOA (SiO_2/Al_2O_3 = 5.5) even at very low pressures (on the order of 10^{-8}). Nitrogen adsorption in the micropores of de-aluminated 390HUA (SiO_2/Al_2O_3 = 400) begins at much higher relative pressures because the number of cation sites that can interact with N_2 quadrupoles is much lower than in 320HOA. The enhancement in 320HOA N_2 loading due to quadrupole-cation interactions persists throughout the micropore-filling pressure range, until the isotherms coincide at a value of a_s close to 1.

Fig. 4 shows that for Ar adsorption at 87.4 K (Fig. 4), by contrast, little difference is found between 320HOA and 390HUA. Micropore filling begins at approximately $p/p_0=10^{-3}$ in both zeolites, and the Ar loadings are similar throughout the micropore-filling pressure range.

Argon adsorption can therefore be used to characterize micropore structure regardless of whether cationic adsorption sites are present. If cation sites are present, they interact

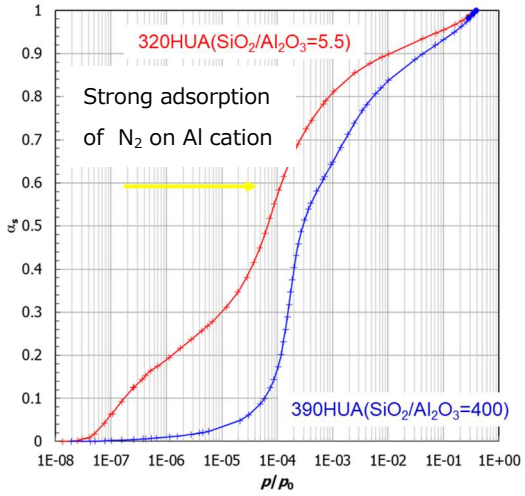

Fig.3 a_s-Curve (N_2@77.4K)

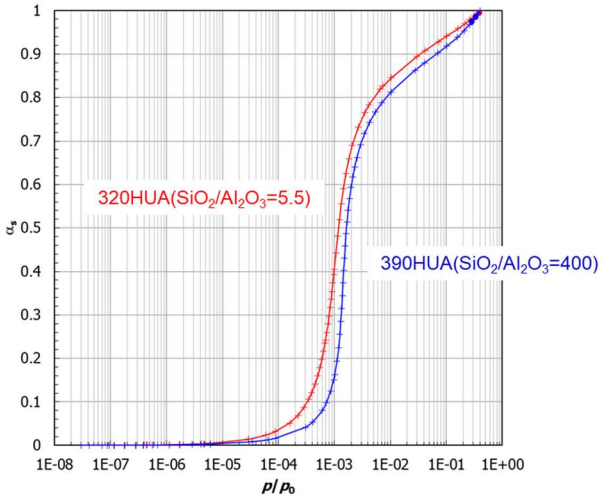

Fig. 4 a_s-curve (Ar@87.3K)

strongly with the quadrupoles in molecular nitrogen and enhance nitrogen loading in the micropore-filling pressure range.

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