

Effects of post-processing treatment on sorption isotherm of an effectively hydrophilic zeolite β

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The effects of post-processing treatments on infiltration and defiltration of liquids in acid-leached zeolite β were investigated. The infiltration pressure, which reflects the effective degree of hydrophobicity of the nanopore surface, and the defiltration pressure, which dominates the system hysteresis, can be controlled in broad ranges by adjusting anion species and liquid composition, and/or performing hydrothermal or silicon addition treatment. These experimental results have important relevance to developing liquid spring and active control techniques.

1. Introduction

Zeolites and zeolite-like materials, also known as molecular sieves, are important microporous materials that have been widely used for catalysis, purification, absorption, among other applications [1]. There are more than 100 different types of natural or synthetic zeolites; most of them have nanopore sizes in the range 0.6–0.9 nm and specific nanopore volumes around 0.2 cm³ g⁻¹ [2]. Compared with other nanoporous materials, such as activated carbons, nanoporous silica gels and nanoporous metals and alloys, zeolites have well-crystallized porous structures [3, 4].

Owing to the confinement effect of nanopore walls, a zeolite does not absorb all the molecules that tend to attach to the nanopore surface. The molecular size must be much smaller than the nanopore size, leaving sufficient space for van der Waals equilibrium distance [5]. However, for some chemicals, even though the molecular sizes are small, if the system free energy increases as they approach the nanopore surface, infiltration still cannot take place, unless external driving forces are applied. For instance, although the size of water molecules is only about 0.3 nm, as the negatively charged defect sites of a zeolite are deactivated, the effective zeolite–water interfacial tension, γ_{zw} , becomes larger than the summation of the surface tensions of zeolite (γ_z) and water (γ_w) [6], and consequently water molecules do not enter the nanopores, unless the capillary effect is overcome by applying an external pressure [7, 8].

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There are two basic methods to adjust the degree of hydrophobicity of zeolites. The first is controlled synthesis. Zeolites are usually processed through templating technique. The network and the template are initially mixed; as they are separated and the template is removed, the nanopores are produced. The properties of the nanopore surface are strongly affected by the silica/alumina (S/A) ratio [9, 10]. Since the aluminium atoms are major sources of hydrophilic sites, the material becomes hydrophobic if the S/A ratio is large. Usually, as the S/A ratio is larger than 18, the zeolite can be regarded as being hydrophobic in gas absorption analysis [11]. When the S/A ratio is 280, a quasi-hydrostatic pressure about 80 MPa must be applied to force liquid water into nanopores [12, 13]. The S/A ratio can be adjusted through acid leaching. By refluxing a zeolite in an acidic solution, aluminium sites can be deactivated. As a result, the material becomes effectively hydrophobic [14].

The degree of hydrophobicity may also be controlled via post-processing treatment. In the current study, we investigate the effects of hydrothermal treatment and silicon addition treatment. The former deactivates hydroxyl groups, and the latter increases local S/A ratio at the nanopore surface. The influence of liquid composition is also analyzed. This study is intended to modify the performance of liquid springs. A liquid spring consists of nanoporous particles suspended in a liquid phase [15, 16]. The nanopore surface must be non-wettable to the liquid. As an external pressure is applied and the liquid is forced into the nanopores, the system shrinks and the mechanical work is stored as the solid–liquid interfacial tension. As the pressure is lowered, the mechanical energy can be converted back. The system is of great potential for energy storage, active control, etc.

2. Experimental

In order to analyze the post-processing treatment effects, we investigated a zeolite β (BEA) obtained from Zeolyst. Its specific surface area was $360 \text{ m}^2 \text{ g}^{-1}$, and the effective pore size was 0.7 nm. The as-received material was hydrophilic, and therefore an acid-leaching treatment was carried out. About 2g of zeolite powders were mixed with $13 \text{ mol} \text{ l}^{-1}$ aqueous solution of nitric acid (HNO₃) or oxalic acid (COOHCOOH) in a round-bottom flask. The mixture was stirred at 80° C for 12 or 24 h, and then cooled in air and washed by cold water. After drying, the acid-leached sample was calcined at 580° C for 10 h in a protective environment of nitrogen.

The acid-leached sample was compressed into discs in a steel mode under 20 MPa. The diameter of the disc was 19 mm, and the mass was 0.3 g. As the disc was immersed in water, it became semi-transparent, i.e. ice-like. The hydrothermal treatment was performed as a zeolite disc was maintained at 650° C in a quartz-tube furnace. At one end of the tube warm water was injected at the rate of $100 \pm 5 \text{ ml h}^{-1}$ by a digital pump. The water evaporated rapidly in the heating zone and the steam continuously flowed across the zeolite disk and was vented from the other end. Before the hydrothermal treatment, some of the acid-leached zeolite β discs were placed in a vertical condenser connected with a round flask filled by SiCl₄. The zeolite discs were separated from the SiCl₄ by glass wool. At the top of the condenser, a drying pipe with desiccant was used to prevent moisture. When the flask

was heated, SiCl₄ vapour was produced and it flowed through the condenser, performing the silicon addition treatment.

The degree of hydrophobicity of the nanopore surfaces of the zeolite β samples was examined through a pressure-induced infiltration experiment. A post-processing treated zeolite disk was immersed in 5g of water or saturated sodium chloride solution in a stainless-steel cylinder. As will be discussed below, the zeolite was hydrophobic and thus the nanopores remained empty under atmosphere pressure. At rest, the liquid phase was pressurized through a steel piston. The piston moved into the cylinder at a slow rate of 0.5 mm min⁻¹, and after the peak load was reached it was moved out at -0.5 mm min⁻¹. The infiltration volume was calculated using $\Delta V_0 - \Delta V_r$, where ΔV_0 is the space occupied by the piston and ΔV_r is the volume variation of a reference system that contained only the liquid phase.

3. Results and discussion

The raw BEA sample is effectively hydrophilic. Owing to the capillary effect, when it is immersed in liquid water, the nanopores are filled immediately. Thus, no pressureinduced infiltration can be observed as an external pressure is applied. As the acidleaching treatment time is longer than about 6 h, the material becomes hydrophobic. Figure 1 shows the sorption isotherm curves of the zeolite samples treated by nitric and oxalic acids for 24 h. The two sorption isotherm curves are quite similar to each other. As the pressure, *P*, is lower than about 20–30 MPa, the system volume decreases quite slowly as *P* increases. The limited infiltration may be related to pressure-aided diffusion of liquid molecules. As the pressure increases, in the range 25–60 MPa, an infiltration plateau is formed. Clearly, the pressure assists liquid molecules to overcome the energy barrier of the hydrophobic nanopore surface. As the liquid enters the nanoporous crystals, the volume of the bulk liquid phase is reduced. The volume change is 150 mm³ g⁻¹, close to but smaller than the theoretical



Figure 1. Sorption isotherm curves of systems treated by nitric and oxalic acids. The liquid phase is modified by sodium chloride.

value of specific nanopore volume ($\sim 200 \text{ mm}^3 \text{ g}^{-1}$), probably due to the van der Waals distance between the liquid molecules and the solid surfaces. After the nanopores are filled, the compressibility of the system is lost, and the slope of sorption isotherm becomes quite large.

Compared with the nanopore size, the NO_3^- anions are quite small, whereas the $C_2O_4^{2-}$ anions are relatively large. Thus, the anion infiltration of nitric acid-leached system should be more pronounced. Note that the infiltration pressures and the infiltration volumes of nitric and oxalic acid-treated zeolites are nearly the same; i.e. the anion influence on infiltration plateau is secondary. As the pressure is reduced, the confined liquid defiltrates out of the nanopores at a low pressure level. As the pressure is lower than about 40 MPa, a defiltration plateau is quite evident. The degree of hysteresis is relatively small, and therefore both systems are suitable to liquid-spring applications. Associated with liquid shrinkage and expansion, mechanical work is stored as or released from solid-liquid interfacial tension over the large nanopore surface, with only a relatively small portion of energy being dissipated. The hysteresis of the oxalic acid-leached system is more pronounced than that of nitric acid-leached one. The difference in defiltration behaviours may be attributed to the different anion sizes of nitric acid and oxalic acid. Since it is easier for NO_3^{-} anions to enter the nanopores, the morphology of acid-leached nanopores as well as the effective density of residual aluminium groups may be different from that of the oxalic acid-modified system, the details of which are still under investigation.

Figure 2 shows the reason why the liquid phase should be a sodium chloride solution. The dashed lines indicate the sorption isotherm curves of reference systems, which are similar to the testing samples except that the liquid phases are pure water. Two types of zeolite β discs are tested. One was treated with nitric acid for 12 h, and the other was treated for 24 h. It can been seen that in either case, with the addition of sodium chloride, whereas the infiltration volume, which reflects the volume of accessible nanopores, remains the same, the infiltration pressure increases, which



Figure 2. Sorption isotherm curves of sodium chloride-modified systems. The solid lines indicate the behaviour of systems based on sodium chloride solution; the dashed lines indicate the behaviour of systems based on pure water.



Figure 3. Sorption isotherm curves of systems modified through various post-treatment procedures. The liquid phase is deionized water.

may be related to the increase in effective liquid polarity. More importantly, the defiltration becomes easier; i.e. the hysteresis of the sorption isotherm decreases, probably caused by the tendency of formation of molecular clusters of water surrounding solvated cations. That is, as the water molecular structure tends to be regular, the lattice resistant is lowered, and consequently with the increase in driving force of defiltration, i.e. the effective degree of hydrophobicity, the liquid "outflow" is promoted.

As the acid-leached zeolite sample is hydrothermally treated, as shown in figure 3, compared with the untreated material (the dashed line) the infiltration pressure increases by about 20%, indicating that the degree of hydrophobicity of nanopore surfaces is higher. The framework aluminium of the zeolite is extracted during the hydrothermal treatment [3]. The water vapour hydrolyzes the Si–O–Al bonds, which results in removal of aluminium groups and formation of hydroxyl nests. Moreover, a relatively small portion of the framework collapses, leading to the formation of more Si–O–Si structures through migration of surrounding SiOH groups or condensation of released SiO₂ and Si(OH)₄ [4], which stabilizes the framework. In figure 3, the liquid phase is deionized water so that the variation in defiltration behaviour can be shown clearly. Associated with the large infiltration pressure, the repelling effect between the solid surface and the confined liquid molecules is more pronounced, so that the difference between infiltration and defiltration pressures is smaller, somewhat similar to the effect of adding sodium chloride.

An even more significant improvement in lowering hysteresis of sorption isotherm is achieved by the SiCl₄ treatment. As the zeolite is exposed to the gaseous SiCl₄, extracted aluminium atoms can be replaced by silicon atoms. That is, SiCl₄ treatment can cause framework dealumination and silicon compensation simultaneously [3]. During the treatment, SiCl₄ molecules are hydrolyzed. The byproduct of hydrochloric acid can further promote the dealumination of the zeolite framework [4]. Residual SiCl₄ and HCl are removed with the gas phase by heating the water in the condenser. After the SiCl₄ treatment, the framework of the zeolite is more perfect. As a result, the infiltration pressure increases by nearly 70% compared with the unmodified material. The infiltration volume does not vary considerably, suggesting that the accessible nanopore structure is not affected. Similar to the phenomena discussed above, the defiltration of confined liquid occurs at a higher pressure as the infiltration pressure increases, leading to the decrease in degree of hysteresis, which can also be related to the high solid–liquid interfacial tension.

4. Concluding remarks

As anion species varies, the effect of acid leaching on infiltration behaviour is not affected, whereas the defiltration pressure may change in a broad range. Through a hydrothermal treatment or a SiCl₄ treatment, the degree of hydrophobicity of an acid-leached zeolite β can be further adjusted. Whereas the volume variation associated with pressure-induced infiltration does not change, the infiltration pressure increases by 20–70%. Compared with hydrothermal treatment, the effect of SiCl₄ treatment is more pronounced. As the solid–liquid interfacial tension rises, defiltration becomes easier and, therefore, the hysteresis of the sorption isotherm is reduced. Similar effects can also be achieved by modifying the liquid phase with sodium chloride.

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