The strong influence of functional structure and cation size on the sorption functionality of trapdoor zeolites

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Keywords: trapdoor behaviour, nuclear energy, gas separation

Trapdoor zeolites such as chabazites (CHA) and merlinoite (MER) (shown in Figure 1a, 1b) with high micro-porosity and thermal controllable cavities have been used in various gas separations involving gases such as CO₂, N₂, and CH₄, and even for the separation of hydrogen isotopes [1-3]. As demonstrated previously, different orientations of functional windows and the size of door-keeping cations lead to very different behaviour during gas sorption, which are not yet well understood [4], inspiring us to study the influence of adsorbing different gases (H₂, D₂, CO₂, and N₂) at various thermal conditions (from room temperature to 80°C) on CHA and MER with different exchanged cations (K⁺ 1.52Å, Rb⁺ 1.67Å and Cs⁺ 1.81Å). The materials were successfully synthesised from zeolite Y followed by facile ion exchange with KCl, RbCl and CsCl, and were characterised by various characterisation techniques including scanning electron microscope (SEM), powder X-ray diffraction (PXRD), simultaneous thermal analysis (STA) and gas sorption.

Figure 1. The SEM pictures for a) CHA and b) MER containing potassium counter cation; framework of c) CHA and d) MER (red bonds represent O and blue bounds for C); e) PXRD patterns for crystals past STA testing up to 500°C; f) Langmuir and BET surface area of MERs and CHAs.

According to STA results, the crystals are stable over 500°C but the smaller (lighter) cation (K⁺ > Rb⁺ > Cs⁺) results in a higher percentage of hydration under the same storage conditions. An increase in around 0.14 Å cation radius (from K⁺ to Cs⁺) leads to around a 5% less water loss. Apart from the cations, the distribution of the functional rings leads to different crystal geometry and different sorption behaviour. CHA crystals grow in all three dimensions forming cubic crystals, but MER crystals only grow in one direction and result in needles (Figure 1c, 1d). Some gas molecules like CO₂ can lower the energy barrier of the trapdoor cations in the eight-member ring (8MR) windows, allowing the gas to pass through the trapdoors into the internal pores, while other gases like N₂ are prevented from entering the internal cavities till the thermal energy of the cation is high enough to open the trapdoor.[4] Moreover, the perpendicular orientation of functional windows in MER causes the space between “doors” in MER to be more likely to be "locked" leading to lower surface area (Table 1) measured by CO₂ and a higher desorption curve compared to the adsorption. This study indicates the high potential of designing temperature swing systems using trapdoor zeolites for various gas separations at milder temperatures.