Discriminative Separation of CO_2 and CH_4 Using a Novel "Molecular Trapdoor" Zeolite: Materials and Process Study

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The efficient separation of CO_2 from natural gas streams is becoming increasingly important as wells containing higher CO_2 content are targeted for LNG production. Conventional techniques for CO_2 removal such as acid gas scrubbing, while effective for low level CO_2 removal, are energy intensive for removal of high CO_2 levels, and can lead to additional environmental problems associated with the solvent. While adsorbents are effective for low level removal of CO_2 at low pressures, an appropriate adsorbent for use at high well head pressure (~ 100 bar) and low to medium CO_2 content has not been identified to date. Existing adsorbents show poor CO_2/CH_4 selectivity at high pressure and high CO_2 level and their use would lead to substantial methane loss.

By conducting a combined experimental (including material synthesis, adsorption characterization, binary breakthrough, Pressure Swing Adsorption process, PALS, NMR, and *in situ* synchrotron powder X-ray diffraction experiment of gas adsorption) and computational (using *ab initio* Density Functional Theory) study, we report on a novel zeolite which is capable of exclusive CO_2 adsorption at high pressure. The zeolite is in the CHA family with Si:Al ratio of 1-3 and contains large cations such as K^+ or Cs^+. We show that these materials are capable of guest-induced cation motion providing access of CO_2 to the internal pore space while preventing access of CH_4. The access is based not on molecular size but rather on the ability of the guest to induce temporary and reversible cation movement. This reversible movement is also temperature dependent. We term it "molecular trapdoor" mechanism (see Figure 1) and provide strong evidence to support this hypothesis through spectroscopic and modeling approaches [1].

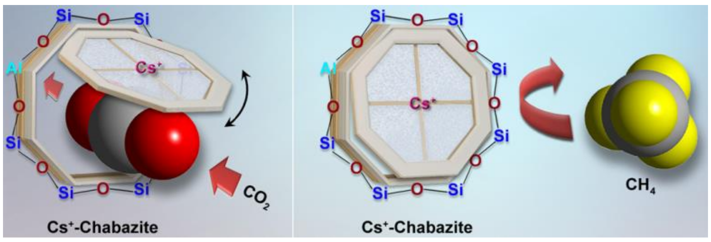

Fig. 1. Schematic representation of the molecular trapdoor for gas discrimination.

Using a 2-bed high pressure PSA apparatus, we demonstrate high methane purity and recovery is attainable provided the temperature of operation is below the temperature at which methane is able to penetrate the zeolite "windows". A methane purity of close to 100% at a recovery of great than 95% is achievable.

[1] J. Shang, G. Li, R. Singh, Q. Gu, K. Nairn, T. Bastow, N. Medhekar, C. Doherty, A. Hill, J. Liu, and P.A. Webley, J. Am. Chem. Soc. **134**, 19246 (2012).