Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for

An Optimal Trapdoor Zeolite for Exclusive Admission of CO_2 at Industrial Carbon Capture Operating Temperatures

Tao Du[a], Xin Fang[ab], Liying Liu*[ac], Jin Shang[d], Bin Zhang[a], Yichao Wei[a], He Gong[a], Shamsur Rahman[c], Eric F. May[c], Paul A. Webley[b], Gang (Kevin) Li*[bc]

[a] State Environmental Protection Key Laboratory of Eco-Industry, School of Metallurgy, Northeastern University, Shenyang, 110819, China. E-mail: liuly@smm.neu.edu.au

[b] Department of Chemical Engineering, The University of Melbourne, Melbourne, Victoria 3010, Australia. E-mail: li.g@unimelb.edu.au

[c] ARC Centre for LNG Futures, The University of Western Australia, 35 Stirling Highway, Crawley, Western Australia 6009, Australia

[d] Joint Laboratory for Energy and Environmental Catalysis, School of Energy and Environment, City University of Hong Kong, Hong Kong SAR, China

Table of Contents

1. DFT Calculations

All results were calculated using the Vienna *Ab initio* Simulation Package (VASP)[1] with the projector augmented waves (PAW) approach.[2] The cut-off energy of the plane wave basis-set was 405 eV. A gamma point only *k*-point mesh was used for one unit cell of chabazite (including three double six-ring prisms or one and a half supercavities). Such cut-off energy and *k*-point mesh have been tested to ensure the total energy value convergence within 1 meV/atom. The atomic positions were optimized with the conjugate gradient method until the forces acting on atoms were below 0.015 eV/Å, as suggested by Göltl and Hafner.[3] To account for the van der Waals interactions, we also adopted the DFT-D3 functional (with IVDW=11). We applied the nudged-elastic-band (NEB) method for energy barrier calculations.

To understand the effect of Si/Al ratio (cation density) on the threshold gas admission temperature, we determined and compared the energy barrier associated with the migration of door-keeping potassium cation (K^+) in **r3**KCHA and **r1**KCHA using density functional theory calculations. Such energy barrier should rely on the affinity of the K^+ to both the starting point and ending point, respectively of the migration pathway. For the same type of cation site (i.e., 8MR, 6MR, or 4MR site), the affinity can be different due to the difference in the number of aluminium atoms contained at this site. A cation site with more aluminum atoms in the ring (thus more negative charge) imparts higher affinity to the K^+ sitting at this site. A zeolite with a Si/Al ratio other than one would have various types of aluminium distribution in the zeolite framework and thus various affinities to the cation for the same type of cation site. In our case, **r1**KCHA has sole aluminum distribution while **r3**KCHA has varied aluminum distribution. Thus when we consider K^+ migration pathway for opening the "door" (i.e., K^+ moves from 8MR site to 4MR site[4]), we need to consider the combinations of different 8MRs and 4MRs in the case of **r3**KCHA. Apart from aluminum distribution, the number of K^+ adjacent to the finishing point of migration (4MR site) will also affect the energy barrier associated with cation migration process, given that these adjacent K^+ will repel the incoming K^+. In the case of **r3**KCHA, the effect of adjacent K^+ is absent since totally 9 K^+ occupies all nine 8MR in one unit cell

and there is no excess K^+ sitting at 4MR site, while there exist excess K^+ cations to occupy 4MR sites in **r1**KCHA. Considering the above two factors – variable aluminium distribution and "adjacent K^+ cations" and to simplify the discussion, we only study the cation migration path associated with the lowest possible energy barrier. For **r1**KCHA, we consider a K^+ migrating from an 8MR site to an adjacent 4MR site with no other adjacent K^+ and the energy barrier is determined to be 1.22 eV (see Figure 1a). For **r3**KCHA, we consider a K^+ migrating from an 8MR site (with only one Al in the ring) to an adjacent 4MR site (with 2 Al in the ring) and the energy barrier is determined to be 0.96 eV (see Figure 1b). We can conclude that potassium chabazite with lower Si/Al ratio imparts higher energy barrier for the migration of door-keeping K^+ and thus higher threshold gas admission temperature. This explains why N_2 and CH_4 are excluded by **r1**KCHA at ambient temperature but admitted by **r3**KCHA.

2. Experiments

Synthesis procedure

The fly ash used in this study was obtained from Shanlu Power Plant, China, and the composition (in wt %) is as follows: Si (22.6 wt %), Al (21.6 wt %), Fe (1.4 wt %), and Ca (2.4 wt %).

The synthesis procedure for chabazite involved two steps viz. fusion and hydrothermal treatment. In a typical procedure, 5 g of fly ash was fused with KOH solid in a tube furnace at 923 K for 1 hour, using the KOH/fly-ash mass ratios of 2.5. Then, 5 g of the resulting product was dissolved in 20 ml water with vigorously stirring for 30 min, followed by ageing for 1 h. Finally, the mixture was transferred into an autoclave and heated at 368 K for 4 days under static conditions. After cooling to the room temperature, the resultant solid was filtered, washed three times with deionized water, and dried at 373 K overnight.

Characterizations

The crystalline properties of the raw materials and the synthesized samples were determined by X-ray diffraction (XRD) using a Shimadzu X-ray diffractometer, with a scanning rate of 2°/min from 4° to 60°. FE-SEM (Field Emission Scanning Electron Microscopy) analysis was conducted by employing a ZEISS scanning electron microscope operated at 15 kV.

Multicomponent breakthrough experiments

Binary breakthrough experiments were examined by a dynamic column breakthrough apparatus,[5] which consists of a stainless steel adsorption column (130 mm long and 22.2 mm internal diameter). Feed gas was flown to the column controlled by four mass flow controllers (MFCs) where a four-way valve controls whether helium (carrier gas) or a combination of helium, CO_2 and nitrogen (or methane). The effluent gas flow rate was measured by an orifice type mass flow meter (MFM) which was then corrected by the on-line gas compositions.

3. Supporting figures

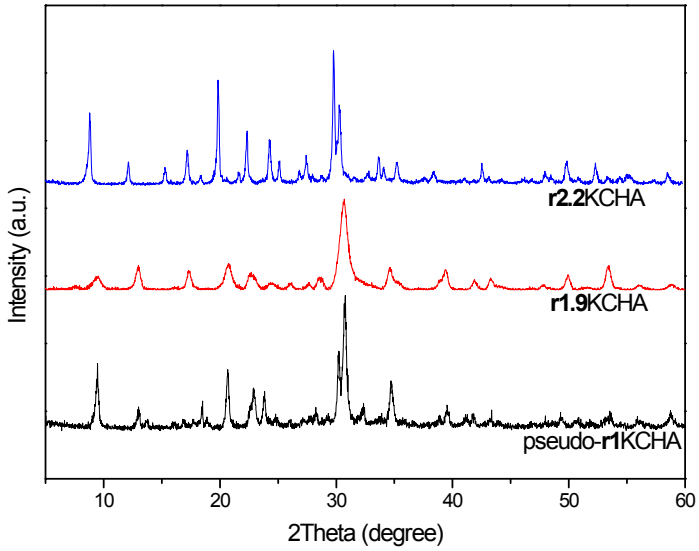

Figure S1 XRD patterns of pseudo-**r1**KCHA, **r1.9**KCHA and **r2.2**KCHA. The pseudo-**r1**KCHA contained amorphous alumina and its real Si/Al ratio was underestimated.

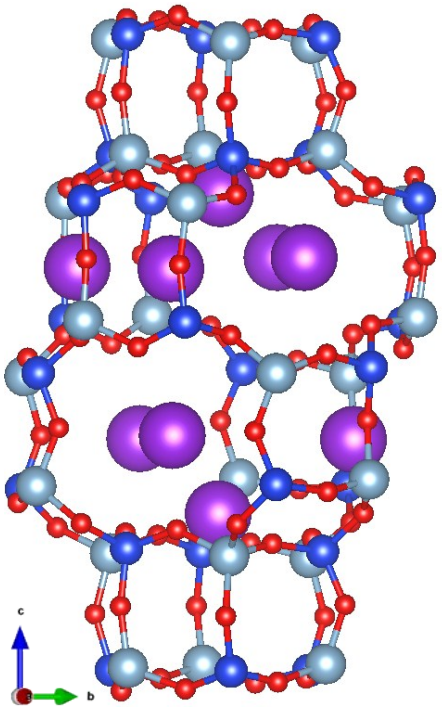

Figure S2 3D structure of a potassium chabazite system.

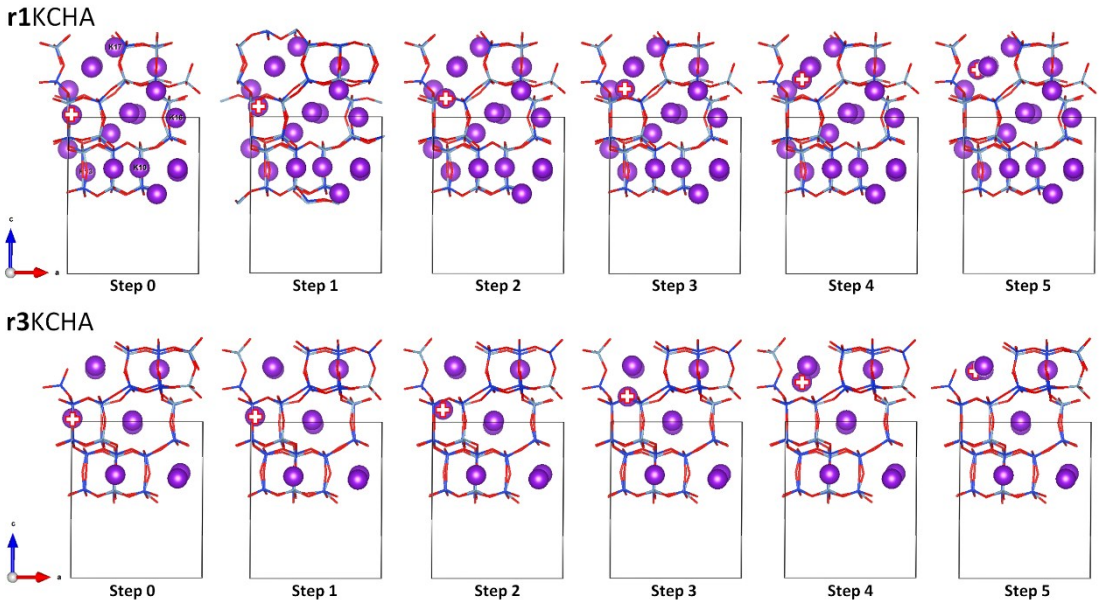

Figure S3 Snapshots of potassium chabazite systems of **r1**KCHA (top) and **r3**KCHA (bottom) during CO_2 adsorption process as calculated by DFT. The migration of the door-keeping potassium cation (marked by the white cross) at different steps was tracked to elucidate the pore opening procedure in these two types of trapdoor chabazites with different cation density.

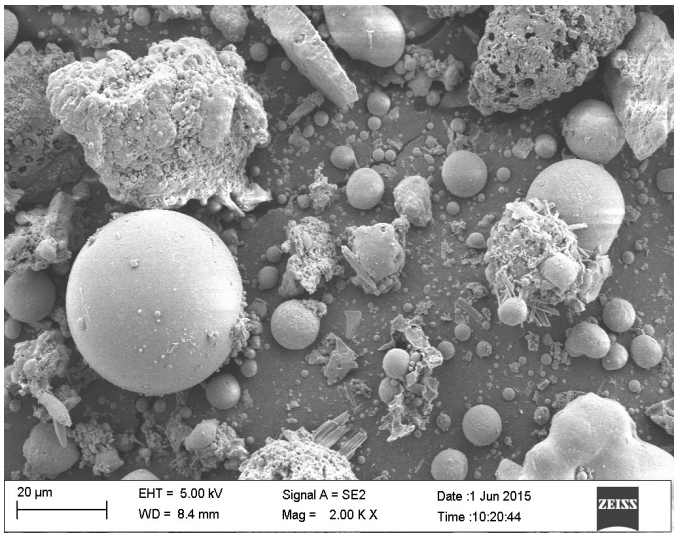

Figure S4 SEM micrograph of fly ash.

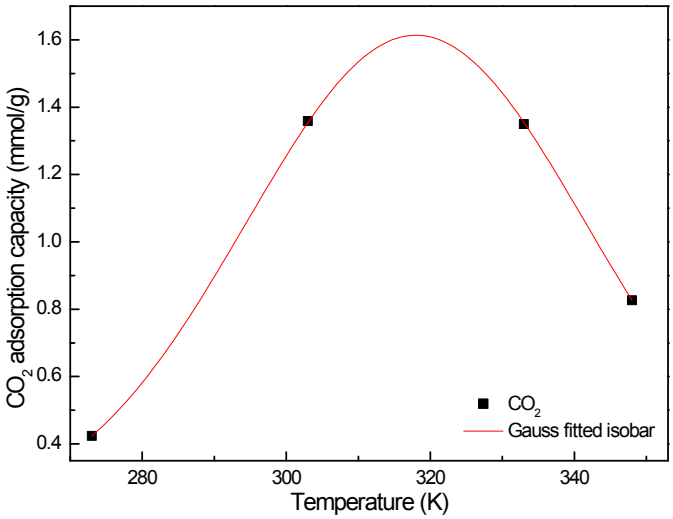

Figure S5 Isobar of as-synthesized **r1.9**KCHA at 0.5 bar.

4. Supporting tables

Table S1 Measured gas adsorption selectivities and capacities on chabazite

Run #	Temperature (°C)	Pressure (bar)	CO_2 Adsorption (mmol/g)	CH_4 Adsorption (mmol/g)	N_2 Adsorption (mmol/g)	Selectivity
#1	30	1	1.0126	n.a.	0.0112	90.41
#2	60	3	0.9654	n.a.	0.0088	109.70
#3	75	1	0.8266	n.a.	0.0012	688.83
#4	30	1	0.9320	0.0016	n.a.	582.50

Reference

1 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169–11186.

2 G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758–1775.

3 F. Göltl and J. Hafner, *J. Chem. Phys.*, 2011, **134**, 1–11.

4 G. K. Li, J. Shang, Q. Gu, R. V Awati, N. Jensen, A. Grant, X. Zhang, D. S. Sholl, J. Z. Liu, P. A. Webley and E. F. May, *Nat. Commun.*, 2017, **8**, 15777.

5 T. L. H. Saleman, G. C. Y. Watson, T. E. Rufford, P. S. Hofman, K. I. Chan and E. F. May, *Adsorption*, 2013, **19**, 1165–1180.