Electronic Supplementary Informatiton for:

Temperature Controlled Invertible Selectivity of Adsorption of N_2 and CH_4 by Molecular Trapdoor Chabazites

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S1. Schematic Representation of Chabazite Structure and Cation Positions

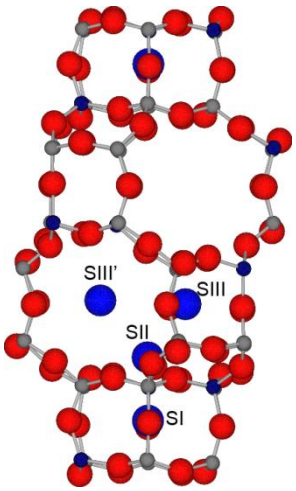

Fig. S1 Schematic representation of chabazite structure and cation positions. Double-six ring prisms (D6Rs) connected by tilted four-membered rings (4MRs) form a three-dimensional structure creating eight-membered rings (8MRs) as the only access to the crystal interior. Four cation sites exist: inside the center of a D6R (SI); inside the supercavity above a D6R (SII); inside the supercavity next to a 4MR (SIII); in the center of an 8MR (SIII').

S2. Computational Set Up for Density Functional Theory (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 Grödtl and Hafner.[3] To take account of the van der Waals interactions in our material systems, we have adopted optB86b.[4-6]

We applied the climbing image nudged-elastic-band (CI-NEB) method for energy barrier calculations.

S3. Site Preference for K cation in r2KCHA

DFT calculations show that the totoal energy of a potassium chabazite with one K at the 8MR doorway (site SIII') is the lowest followed by site SII, suggesting site SIII' is the most preferred position and site SII is the second preferred position.

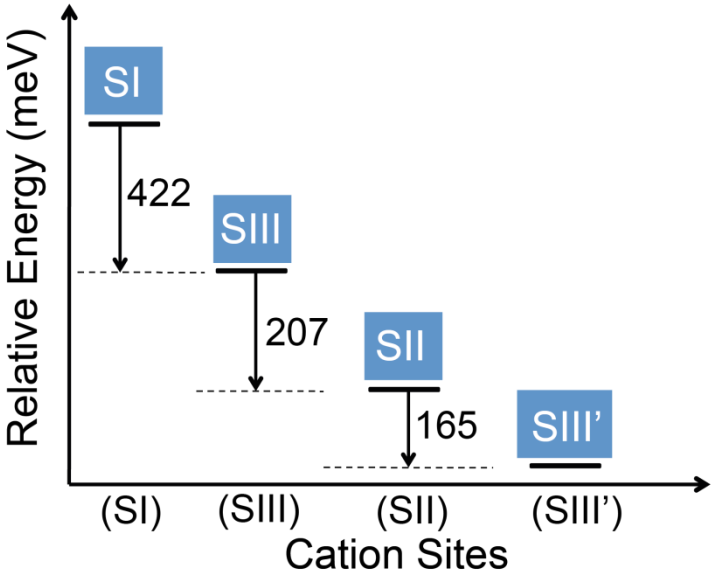

Fig. S2 Relative total energy of a potassium chabazite with one K cation at different sites. Site SIII' associates with the lowest total energy, representing the most stable cation site for K.

S4. *In Situ* Synchrotron PXRD of Adsorption Experiments

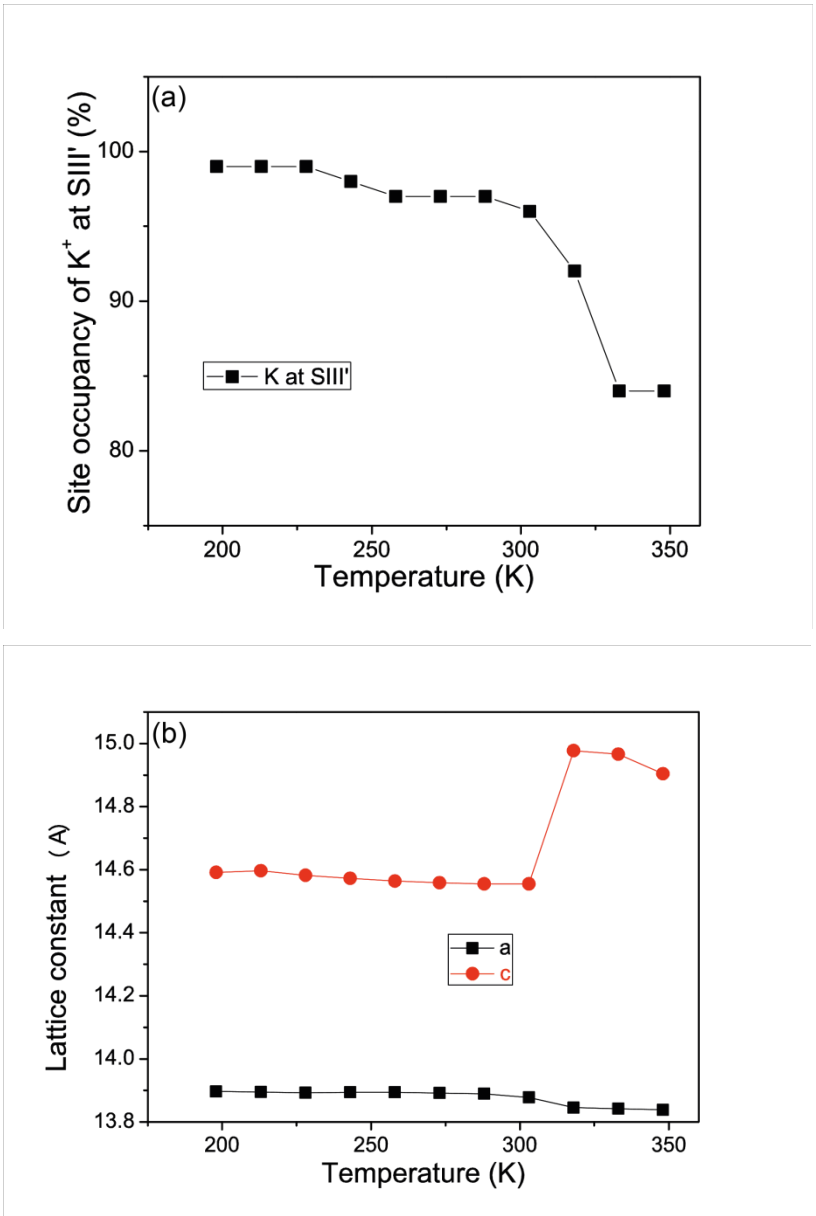

Fig. S3 Evolution of K^+ occupancy at SIII' and lattice constant with temperature. (a) Above 303-313 K, SIII' site occupancy reduces from 100%, leading to the opening of pore apertures. (b) Above 303 K, lattice constant ***a*** starts to decline and ***c*** to incline indicating cation migration. The estimated error in site occupancy is 3% and in lattice constant is 0.2%. Lines are guides to the eye.

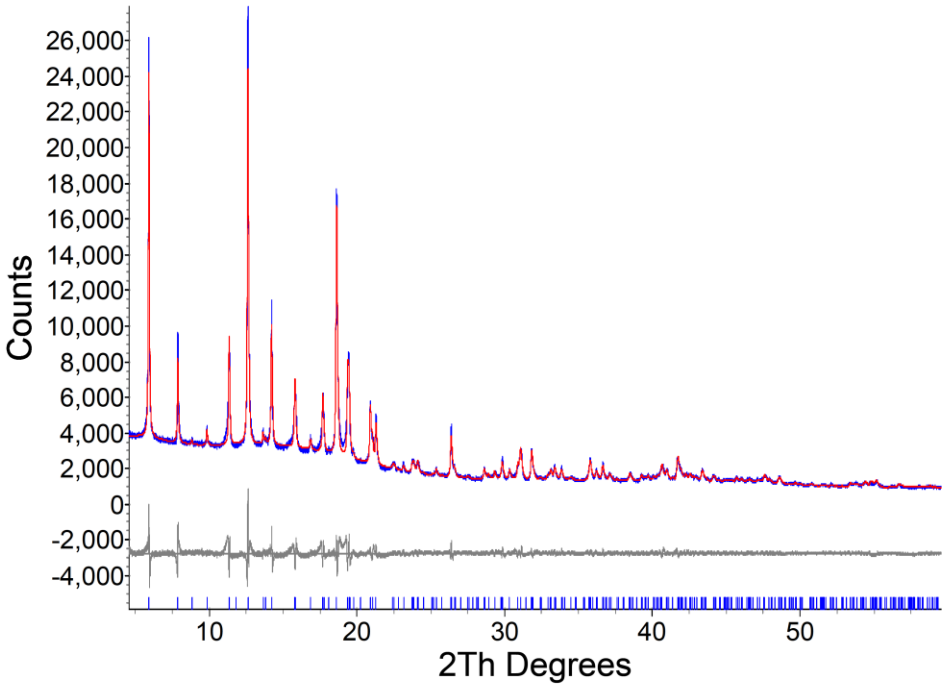

Fig. S4 Rietveld refinement profile for chabazite (**r2**KCHA) phase under CO_2 atmosphere at 303 K. Observed (blue), calculated (red), difference (grey) plots. The refined agreement factors are *R*wp = 5.5 %, R_B = 4.9 % and *GoF*= 2.16. λ = 0.9535 Å. Note that the temperature at which cation occupancy substantially changes (denoting cation migration) is independent of the atmospheres as verified in the case of **r2**CsCHA;[7] therefore we reasonably employed the synchrotron data under CO_2 to study the temperature dependence of cation occupancy in **r2**KCHA.

Table S1. Summary of experiment and crystallographic details for chabazite (**r2**KCHA) phase (rhombohedra setting) under CO_2 at 303K.

Parameters	values
Formula sum	Si3.72 Al8.28 O24 K3.6
Formula weight	852.624 g/mol
Crystal system	trigonal
Space-group	R-3 m (166)
Cell parameters	a=9.3588(2) Å, α=95.6337(15)°
Cell volume	806.98(6) $Å^3$
Z	1
Calc. density	1.75437 g/cm^3
2theta, deg	2θ min = 4, 2θ max = 84

Detector	Mythen-II, Australian Synchrotron
Wavelength	0.9535 Å
R_B	4.9 %
R_{wp}	5.5 %
GoF	2.16

Table S2. Atomic coordinates following refinement of chabazite (**r2**KCHA) under CO_2 at 393K.

Atom	**Wyck. site**	**S.O.F.**	***x*/*a***	***y*/*b***	***z*/*c***
Si	12*i*	0.31	0.1004(6)	0.3333(3)	0.8780(7)
Al	12*i*	0.69	0.1004(6)	0.3333(3)	0.8780(7)
O1	6*f*	1	0.2443(5)	-0.2443(5)	0
O2	6*g*	1	0.1182(3)	-0.1182(3)	½
O3	6*h*	1	0.2930(8)	0.2930(8)	0.8831(4)
O4	6*h*	1	0.0315(6)	0.0315 (6)	0.3118(9)
K1	3*e*	0.96	0	½	½
K2	2*c*	0.36	0.2388(13)	0.2388(13)	0.2388(13)

S5. Binding Energies for N_2 and CH_4 on r2KCHA Calculated by DFT

In our *ab initio* simulations, the K form chabazite with Si/Al ratio of 3 (**r3**KCHA) was constructed to represent a typical high cation density chabazite (nine cations per unit cell);[8] To study the interactions between the chabazite and the guest gas molecules, a single gas molecule was placed close to the K^+ cations (one gas molecule per unit cell), and then the complex was fully relaxed *via* the conjugate gradient algorithm. The adsorption energy (calculated at 0 K) of different guest gas molecules is defined as the difference between the total energy of the chabazite–gas molecule adsorption complex and the total energy of chabazite (CHA) augmented by the energy of the isolated single gas molecule: $E_{ads} = E_{tot}(\text{CHA+gas}) - E_{tot}(\text{CHA}) - E_{tot}(\text{gas})$.

S6. References

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