Supporting Information

Revealing CO_2 Adsorption Blocking Mechanism in Flexible Low-Silica Small-pore Zeolites via Three-Dimensional Electron Diffraction

Jian Guo[a,b], Chenyang Nie[b,c], Shitai Li[b,c], Nana Yan[b*], Peng Guo[b,c*], Zhongmin Liu[a,b,c]

a. Henan Institute of Advanced Technology, Zhengzhou University, Zhengzhou 450001, China.
b. National Engineering Research Center of Lower-Carbon Catalysis Technology, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China.
c. University of Chinese Academy of Sciences, Beijing 100049, China.

Materials

Aluminium hydroxide (99.6 %, Aladdin Chemistry Co., Ltd.), Ludox HS-40 (40 %, Aldrich; suspension in water), Sodium hydroxide (98 %, Aladdin Chemistry Co., Ltd.), NaY zeolites (Nankai University Catalyst Co., Ltd), Potassium hydroxide (85 %, Damao Chemical Reagent Factory), Sodium chloride (Tianjin Fuchen Chemical Reagent Factory), Potassium chloride (Guangdong Guanghua Sci-Tech Co., Ltd). All reagents were used without purification.

Zeolites synthesis and Ion-exchange

The synthesis of Na-GIS was based on a reported recipe in the literature,[1] with some modifications. In the typical synthesis of Na-GIS, 0.98 g NaOH was added to 6.65 g deionized water and stirred to dissolve. Then, 0.20 g $Al(OH)_3$ was added and stirred for 1 h. Subsequently, 1.54 g Ludox HS-40 was added and stirred overnight to form a homogeneous gel with a molar ratio of $4.68Na_2O$: $1.0Al_2O_3$:8 SiO_2:184 H_2O. The gel was transferred into a 50 mL Teflon-lined stainless-steel autoclave and crystallized at 100 °C under rotation at 50 rpm for 72 h. The final Na-GIS was obtained by centrifugation, repeated washing with deionized water, and drying at 100 °C overnight.

K-GIS was prepared by ion exchange of Na-GIS. Na-GIS was fully converted to the K form using 1 M KCl solution at room temperature for 4 h, repeated three times. The resulting K-GIS was obtained by centrifugation, repeated washing with deionized water, and drying at 100 °C overnight.

PHI-type zeolite was synthesized using both K^+ and Na^+ ions. Specifically, 0.12 g NaOH and 0.12 g KOH were dissolved in 2.28 g deionized water, followed by the addition of 0.72 g NaY zeolite. The mixture was stirred for 5 h, forming a uniform gel with a molar ratio of $1.8Na_2O$: $0.6K_2O$: $1.0Al_2O_3$:5 SiO_2:81.3 H_2O. This gel was transferred into a 50 mL Teflon-lined stainless-steel autoclave and crystallized at 100 °C for 72 h. The final product was obtained by centrifugation, repeated washing with deionized water, and drying at 100 °C overnight.

Na-PHI and K-PHI were prepared by ion exchange of the above **PHI** zeolite. The zeolite was exchanged into the Na or K form using 1 M NaCl or KCl solution, respectively. K-PHI was prepared by two exchanges at room temperature, each lasting 6 h, while Na-PHI was prepared by seven exchanges at 80 °C, each also lasting 6 h. The final products were obtained by centrifugation, repeated washing with deionized water, and drying at 100 °C overnight. After the exchange, Na-PHI still contained a small amount of K^+ (Table S1), but all ions were treated as Na^+ during structural refinement.

Characterization

PXRD data were collected using a PANalytical X'Pert PRO X-ray diffractometer (Cu Kα, λ = 1.5418 Å) for phase analysis. SEM images were taken through a Hitachi SU8020 microscope. Chemical composition was determined using a PANalytical Axios advanced X-ray Fluorescence Spectrometer. CO_2, N_2 and CH_4 adsorption/desorption isotherms were performed on a Micrometrics 3FLEX instrument. Before tests, all the samples were degassed at 350 °C for 4 h under vacuum. Isotherms were measured at 25 °C and the equilibration interval of each point was set to 40 s.

Structural Analysis

cRED data were collected on a JEOL 2100 Plus TEM equipped with an ASI Cheetah120 detector. The raw data were analyzed using the X-ray Detector Software (XDS)[2]. The initial structural models were solved by using SHELXT[3], and the subsequent determination of cation locations and structure refinement were conducted by using SHELXL[3].

Theoretical calculation

The molecular dynamics annealing simulations[4] were performed by placing 19 CO_2 molecules into 2×2×2 unit cells. The Universal Force Field was used for the simulation. The annealing process was conducted with a maximum temperature of 227 °C and a target temperature of 27 °C for a total of 50 cycles, with five ramps performed in each cycle. Each ramp allowed 100 dynamic steps, for a total of 50,000 steps.

Breakthrough experiments

Breakthrough experiments for CO_2/CH_4 and CO_2/N_2 mixtures were performed on BSD-MAB instrument from Beishide Instrument Technology (Beijing) Co., Ltd. The samples were loaded into the quartz tube with a diameter of 2 mm. Before tests, the samples were activated at 350 °C under vacuum for 4 h. All tests were carried out at 25 °C and 1bar with a flow rate of 5 mL/min. Argon (5 ml/min) was used as the reference gas to stabilize the gas flow and was directed through a separate tube, bypasses the sample bed. The outlet gas mixture was detected by a mass spectrometer.

Table of Contents

Figures

Table S1. Chemical compositions of four types of zeolites in this work measured by XRF.

Samples	Unit cell compositions
Na-GIS	$\|Na_{5.8}\|[Si_{10.2}Al_{5.8}O_{32}]$
K-GIS	$\|K_{5.8}\|[Si_{10.2}Al_{5.8}O_{32}]$
Na-PHI*	$\|Na_{5.5}K_{0.4}\|[Si_{10.1}Al_{5.9}O_{32}]$
K-PHI	$\|K_{5.8}\|[Si_{10.2}Al_{5.8}O_{32}]$

*：Na-PHI contained a small amount of K^+ ions， which were ignored during the structural refinement process.

Table S2. The cRED details of structural refinement for Na-GIS-DH.

Sample	Na-GIS-DH
Tilt range (°)	-43~64.9
Exposure time/frame (s)	0.3
Number of frames	244
Crystal system	Tetragonal
Space group	$P4_12_12$
a (Å)	9.6
b (Å)	9.6
c (Å)	8.9
α (°)	90.0
β (°)	90.0
γ (°)	90.0
V (Å³)	823.7
Resolution (Å)	0.84
Completeness (%)	99.6
R_{int} (%)	16.29
Unique Reflections Fo > 4sig (Fo)	423
Parameters	67
Restraints	67
R_1	0.1292
GOF	1.111
CCDC number	2385940

Table S3. The cRED details of structural refinement for K-GIS-DH.

Sample	K-GIS-DH
Tilt range (°)	-59.9~62.1
Exposure time/frame (s)	0.3
Number of frames	272
Crystal system	Tetragonal
Space group	$I4_1/a$
a (Å)	9.7
b (Å)	9.7
c (Å)	9.4
α (°)	90.0
β (°)	90.0
γ (°)	90.0
V (Å³)	891.9
Resolution (Å)	0.84
Completeness (%)	99.5
R_{int} (%)	14.97
Unique Reflections Fo > 4sig (Fo)	260
Parameters	39
Restraints	1
R_1	0.1222
GOF	1.183
CCDC number	2385938

Table S4. Breakthrough results of CO_2/CH_4 （5/95，v/v） and CO_2/N_2 （15/85，v/v） on K-GIS at 25 °C and 1 bar with a total flow rate of 5 ml/min.

Binary mixture	Saturated Adsorption Capacity (mmol/g)			Separation Coefficient
	CO_2	N_2	CH_4	
CO_2/N_2	1.8	0.2	-	50.7
CO_2/CH_4	1.8	-	≈ 0	Infinite

Table S5. The cRED details of structural refinement for Na-PHI-DH.

Sample	Na-PHI-DH
Tilt range (°)	-63.2~57.2
Exposure time/frame (s)	0.3
Number of frames	266
Crystal system	Monoclinic
Space group	$P2_1/m$
a (Å)	8.1
b (Å)	13.1
c (Å)	8.1
α (°)	90.0
β (°)	106.7
γ (°)	90.0
V (Å³)	822.8
Resolution (Å)	0.95
Completeness (%)	86
R_{int} (%)	18.06
Unique Reflections Fo > 4sig (Fo)	555
Parameters	143
Restraints	2
R_1	0.1695
GOF	1.508
CCDC number	2402481

Table S6. The ion occupancy and multiplicity at different 8-rings in PHI-type zeolites.

Samples	Site I		Site II		Site III		Site IV		Total atom per unit cell
	Occ[a]	Mul[b]	Occ[a]	Mul[b]	Occ[a]	Mul[b]	Occ[a]	Mul[b]	
Na-PHI-DH	0.42	2	1.00	2	0.46	4	0.61	2	5.9
K-PHI-DH	0.73	2	0.86	2	0.50	4	0.27	2	5.72

[a] refers to occupancy.
[b] refers to multiplicity.

Table S7. The cRED details of structural refinement for K-PHI-DH.

Sample	K-PHI-DH
Tilt range (°)	-69.9~37.4
Exposure time/frame (s)	0.3
Number of frames	239
Crystal system	Monoclinic
Space group	$P2_1/m$
a (Å)	8.3
b (Å)	13.5
c (Å)	8.3
α (°)	90.0
β (°)	108.2
γ (°)	90.0
V (Å³)	875.7
Resolution (Å)	0.84
Completeness (%)	73.3
R_{int} (%)	10.33
Unique Reflections Fo > 4sig (Fo)	810
Parameters	144
Restraints	1
R_1	0.1655
GOF	1.687
CCDC number	2385939

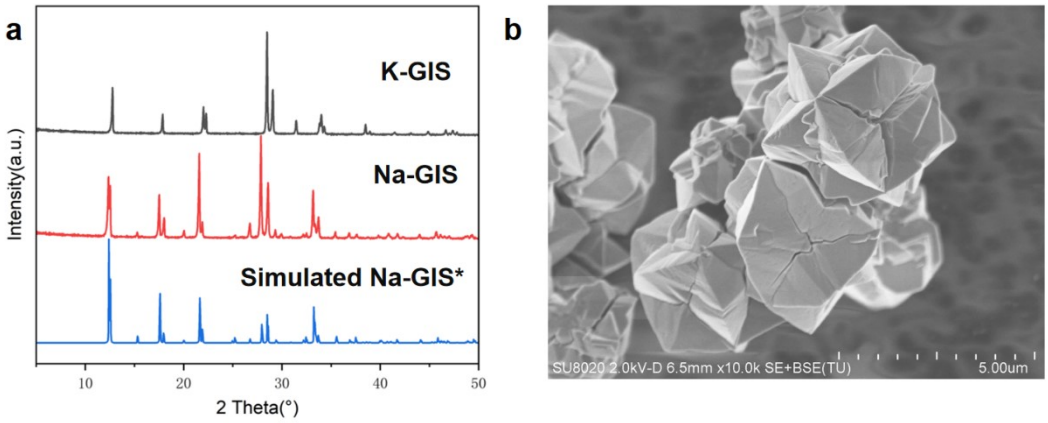

Fig. S1. (a) PXRD patterns of **GIS**-type zeolites. (b) SEM image of as-synthesized Na-GIS.

*: The simulated PXRD pattern of Na-GIS is derived from the reported structure in the reference.[5]

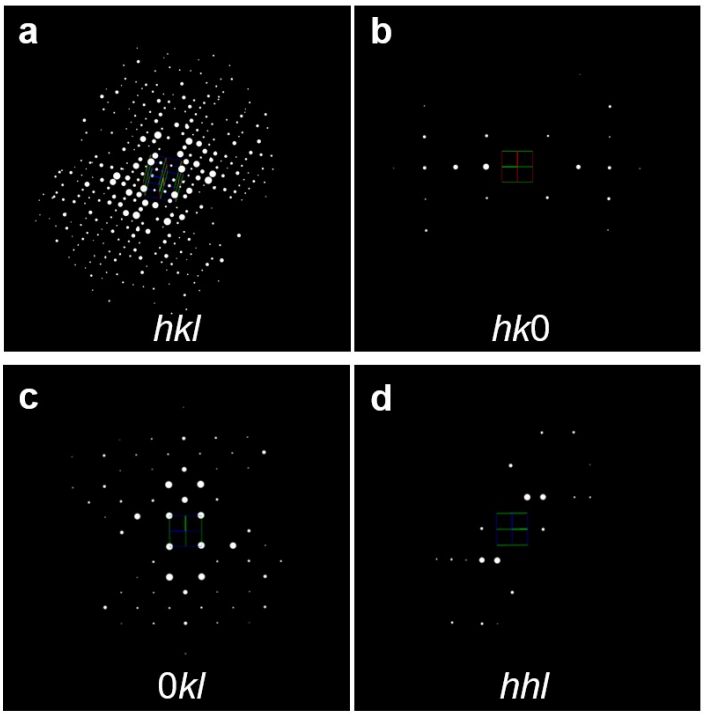

Fig. S2. (a) 3D reciprocal lattice of K-GIS-DH. (b-d) Three slices of *hk*0, 0*kl*, and *hhl* extracted from the reconstructed reciprocal lattice.

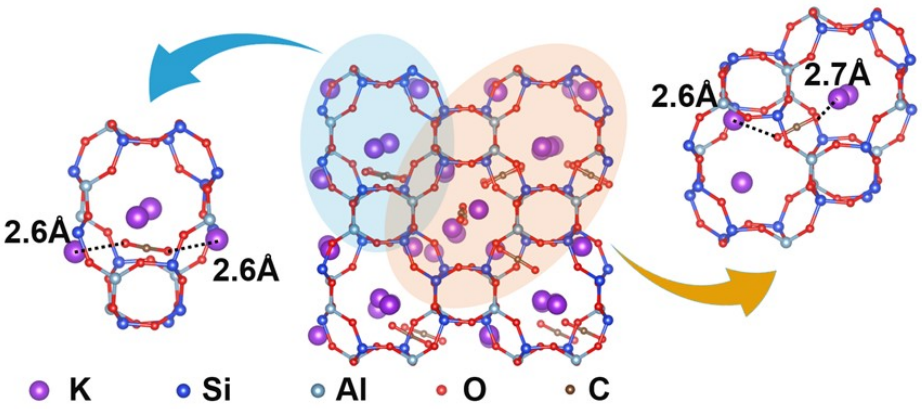

Fig. S3. CO_2 adsorption sites in K-GIS by theoretical calculation.

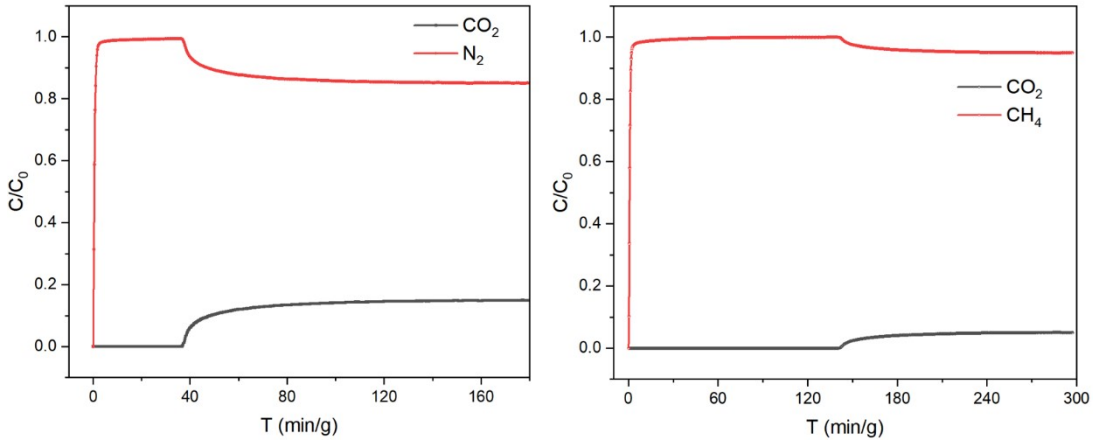

Fig. S4. Experimental binary breakthrough curves for a gas mixture of CO_2/N_2 (15/85, v/v) (left) and CO_2/CH_4 (5/95, v/v) (right) on K-GIS at 25 °C and 1 bar with a total flow rate of 5 ml/min.

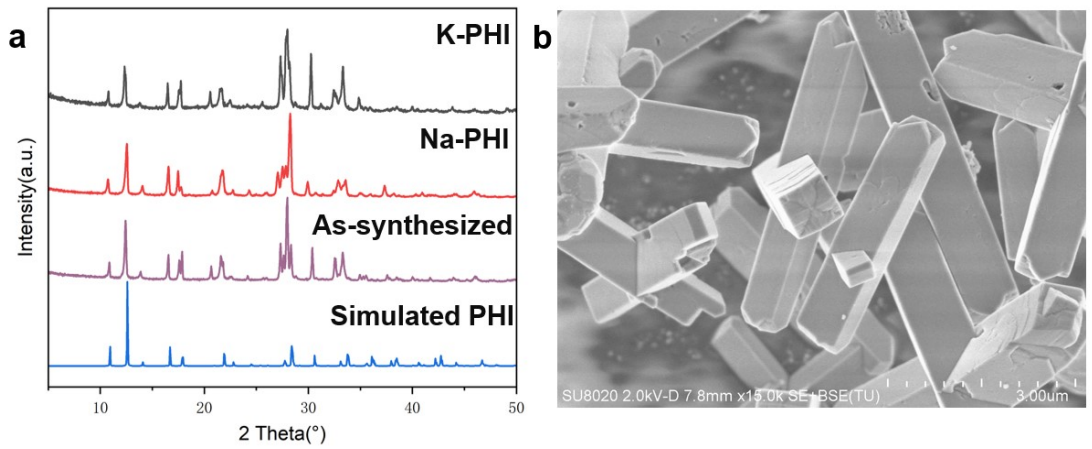

Fig. S5. (a) PXRD patterns of **PHI**-type zeolites. (b) SEM image of as-synthesized PHI.

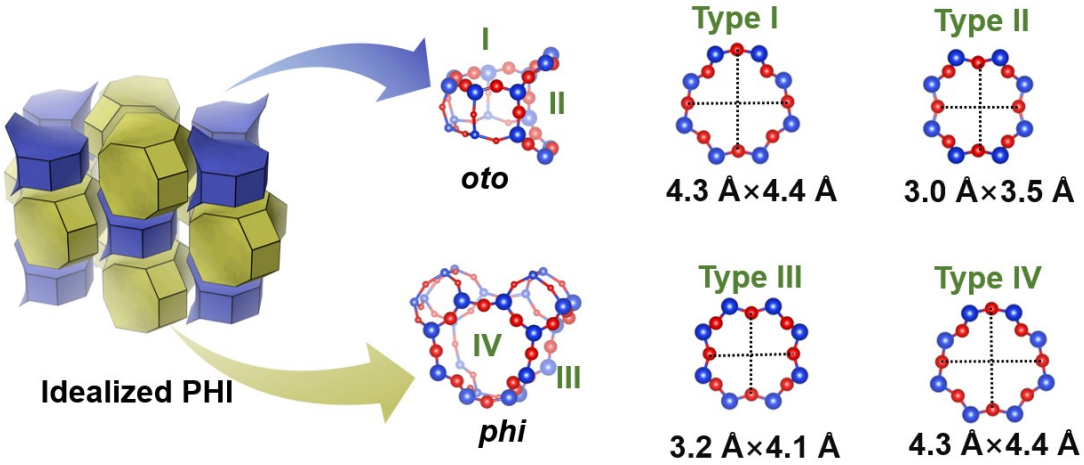

Fig. S6. The tiling structure of idealized **PHI**-type framework (left), *oto* and *phi* CBUs (middle), 8-ring pore openings (right).

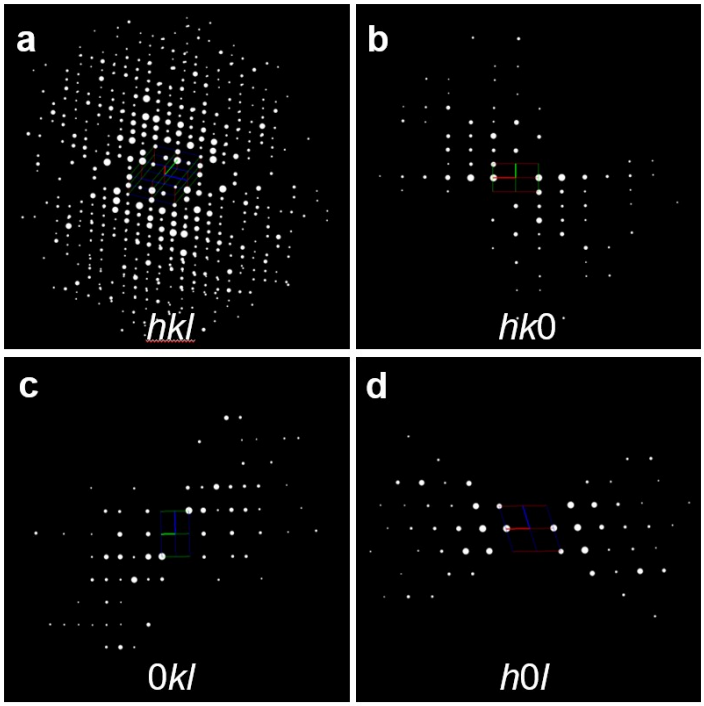

Fig. S7. (a) 3D reciprocal lattice of Na-PHI-DH. (b-d) Three slices of *hk*0, 0*kl*, and *h*0*l* extracted from the reconstructed reciprocal lattice.

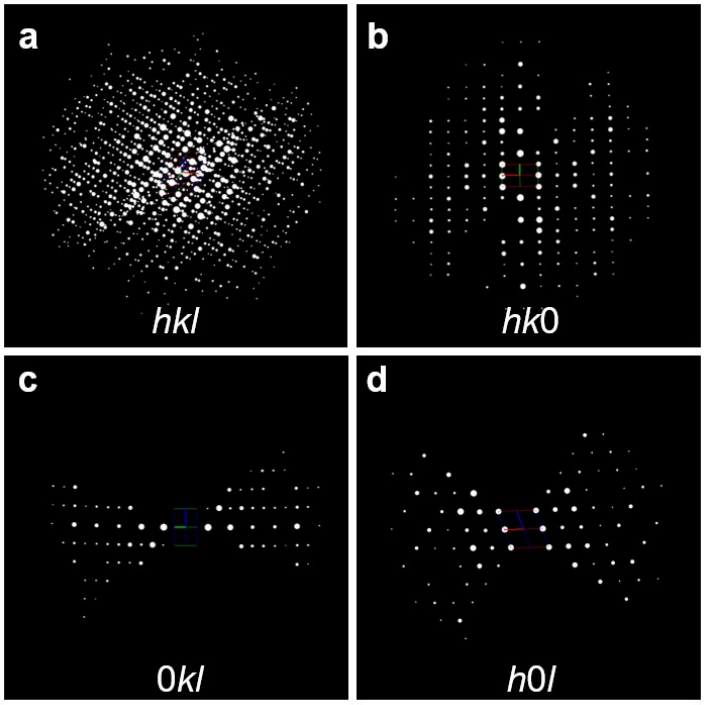

Fig. S8. (a) 3D reciprocal lattice of K-PHI-DH. (b-d) Three slices of *hk*0, 0*kl*, and *h*0*l* extracted from the reconstructed reciprocal lattice.

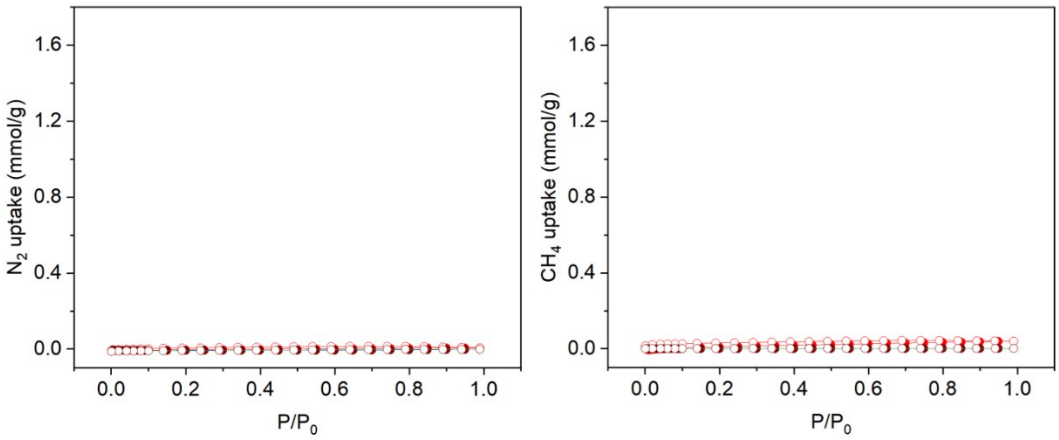

Fig. S9. N_2 (left) and CH_4 (right) adsorption isotherms of K-GIS (brown) and K-PHI (red) at 25 °C.

Reference

1. M. D. Oleksiak, A. Ghorbanpour, M. T. Conato, B. P. McGrail, L. C. Grabow, R. K. Motkuri and J. D. Rimer, *Chem. Eur. J*, 2016, **22**, 16078-16088.
2. W. Kabsch, *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, 2010, **66**, 125-132.
3. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2007, **64**, 112-122.
4. P. Krokidas, E. D. Skouras, V. Nikolakis and V. N. Burganos, *Mol. Simul.*, 2008, **34**, 1299-1309.
5. S. Hansen, U. Hakansson and L. Falth, *Acta Crystallogr. C Struct. Chem.*, 1990, **46**, 1361-1362.