## Multifunctional Petrochemical Separation Adsorbent Based on Micro-Regulation of Cu-BTC Channel

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#### Abstract

Separating hydrocarbons from refinery dry gas is a fundamental demand in petrochemical industry. Metal-Organic Frameworks are a class of promising advanced adsorbents, yet better moisture stability and higher adsorptive selectivity are still needed to meet the requirement of petrochemical industry. Herein, a multifunctional adsorbent urea@Cu-BTC was prepared from cheap building blocks at room temperature, which exhibits generally enhanced adsorptive separation performance towards CO2/CH4, CO2/N2, C3H6/C3H8, C2H4/C2H6, CH4/N2 separation. More interestingly, urea@Cu-BTC shows significantly enhanced stability against moisture. Combining structural characterization and molecular simulation, the improved adsorptive separation performance was ascribed to the enhanced confinement from the creation of ultra-micro porosity due to the presence of urea molecule in the microporous channel of Cu-BTC. The major components in refinery dry gas can be well separated using a column filled with urea@Cu-BTC, which demonstrates that micro-regulating the channel of MOFs is a feasible strategy for preparing high performance petrochemical adsorbents.













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# Multifunctional Petrochemical Separation Adsorbent Based on Micro-Regulation of Cu-BTC Channel

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## Abstract

Separating hydrocarbons from refinery dry gas is a fundamental demand in petrochemical industry. Metal-Organic Frameworks are a class of promising advanced adsorbents, yet better moisture stability and higher adsorptive selectivity are still needed to meet the requirement of petrochemical industry. Herein, a multifunctional adsorbent urea@Cu-BTC was prepared from cheap building blocks at room temperature, which exhibits generally enhanced adsorptive separation performance towards CO<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/N<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>, CH<sub>4</sub>/N<sub>2</sub> separation. More interestingly, urea@Cu-BTC shows significantly enhanced stability against moisture. Combining structural characterization and molecular simulation, the improved adsorptive separation performance was ascribed to the enhanced confinement from the

creation of ultra-micro porosity due to the presence of urea molecule in the microporous channel of Cu-BTC. The major components in refinery dry gas can be well separated using a column filled with urea@Cu-BTC, which demonstrates that micro-regulating the channel of MOFs is a feasible strategy for preparing high performance petrochemical adsorbents.

KEYWORS: adsorption/gas; refinery dry gas; channel regulation; moisture stability; metal-organic framework

## **1. Introduction**

Petroleum, the predominant raw material of many valuable chemicals, is considered as the "industry blood". Catalytic cracking of petroleum yields the mixture of lighter products (Scheme 1), including propane, propylene, ethane, ethylene, methane, carbon dioxide, etc.<sup>[1]</sup> Hence, it is of industrial significance to separate hydrocarbons from the mixture for the purified products such as polymer grade olefins. Table 1 lists the composition of a typic refinery dry gas<sup>[2]</sup>. After desulfurization, the treatment of sweet gas mainly includes the following 6 steps:

- A. **CO<sub>2</sub> stripping**, which comes down to the separation of CO<sub>2</sub> from N<sub>2</sub> and CH<sub>4</sub> under moisture.
- B. C2-C3 recovery, which concerns the extraction of C2-C3 from CH<sub>4</sub>.
- C. C<sub>3</sub>H<sub>6</sub> recovery, where the key is selective separation of  $C_3H_6$  from  $C_3H_8$ .
- D. C<sub>2</sub>H<sub>4</sub> recovery, where the key is selective separation of  $C_2H_4$  from  $C_2H_6$ .

- E. CH<sub>4</sub> recovery, where the main challenge is efficient extraction of  $CH_4$  from  $N_2$ .
- F. H<sub>2</sub> production, which separates  $H_2$  from  $N_2$  and  $O_2$ .

Despite the wide deployment of distillation technology for this application, the harsh working conditions of high pressure (7-28 bar), low temperature (183-258 K), extreme reflux ratio (up to ~20), and numerous plate number (>100) lead to the intensive consumption of energy<sup>[3]</sup>. As a result, the heat-driven chemical separation processes account for ~50% of US industrial energy consumption<sup>[4]</sup>. On the contrary, adsorptive separation technology emerged as a promising alternative to distillation due to its inherent mild working conditions and low consumption of energy<sup>[5-7]</sup>. The design and preparation of advanced adsorbents with superior selectivity, decent capacity, reliable regeneration, and good stability are the key to efficient separation and purification processes<sup>[8]</sup>. The main challenge arises from similar molecular size and polarization of the hydrocarbon analogs to be separated (Table 1)<sup>[2, 9]</sup>.



Scheme 1 Scheme of the separation process for refinery dry gas

Composition	Content	Kinetic	Polarization	Composition	Content	Kinetic	Polarization
	(%)	diameter/Å	$\times 10^{25}$ /cm <sup>3</sup>		(%)	diameter/Å	$\times 10^{25}$ /cm <sup>3</sup>
CO <sub>2</sub>	2.08	3.3	29.11	$C_2H_4$	16.38	4.16	42.52
CH4	31.38	3.76	25.93	$C_2H_6$	14.91	4.44	44.3-44.7
$N_2$	20.40	3.64-3.80	17.40	$C_3H_6$	0.90	4.68	62.6
$H_2$	12.35	2.83-2.89	8.04	$C_3H_8$	0.14	4.3-5.12	62.9-63.7
$O_2$	0.74	3.47	15.81	H <sub>2</sub> O	0.72	2.64	14.5

Table 1 The composition of a typical refinery dry gas

Conventional adsorbents such as zeolites<sup>[10-12]</sup>, activated carbons<sup>[13, 14]</sup> and aluminum oxide<sup>[15]</sup> have been investigated in gas separation. Metal-Organic Frameworks (MOFs) have been broadly used in hydrocarbons separation due to the merits of flexible structure, well-developed porosity, and tunable framework<sup>[16-18]</sup>. In particular, Cu-BTC exhibits high adsorptive capacity at ambient conditions<sup>[19-21]</sup>, and has been commercialized by BASF (Basolite<sup>®</sup> C300)<sup>[22]</sup>. Cu-BTC has paddle-wheel type metal corners bounded to four tricarboxylate linkers that bears different microporous cages with the pore size of 3.5 Å and 9 Å<sup>[23]</sup>, respectively. Besides, unsaturated Cu acts as Lewis-acid site to polarize adsorbates, facilitating enhanced adsorption toward olefins and CO2. However, the unsaturated Cu sites are also vulnerable to moisture attack<sup>[24, 25]</sup>. Great effort has been devoted to improve the separation performance and moisture stability of MOFs. Li et al.<sup>[26]</sup> protected Cu-BTC with imidazole to synthesize Imi@Cu-BTC, which exhibited enhanced moisture stability at the cost of slight loss in CO<sub>2</sub> capacity. Lin et al.<sup>[27]</sup> proposed the postsynthetic preparation of ACN@Cu-BTC, which achieved the complete preservation of CO2 capacity under moisture. Wu et al.<sup>[28]</sup> developed the bifunctional SBU-tuning strategy (SBU: Secondary Building Unit) to synthesize Gly@Cu-BTC, exhibiting enhanced CO<sub>2</sub> uptakes (5.4 mmol/g), CO<sub>2</sub>/CH<sub>4</sub> selectivity (8.53), CO<sub>2</sub>/N<sub>2</sub> selectivity (59.38), and moisture stability (up to 20 days) at 298 K and 1 bar simultaneously. Sun et al. grafted pyrrole onto Cu–BTC to prepare Pyr@CuBTC, which showed high C<sub>3</sub>H<sub>6</sub> capacity (7.60 mmol/g) and C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> selectivity (8.3) at ambient condition. Despite progresses in these specific applications, a generalized strategy for the preparation of multifunctional petrochemical separation adsorbents is needed to avoid expensive and time-consuming adsorbent design and synthesis for each of these specific separation progresses. Herein, we propose the SBU-tuning strategy to micro-regulate the channel of Cu-BTC, which simultaneously improves the capacity, selectivity, regeneration, and stability of the Cu-BTC derived adsorbent urea@Cu-BTC for CO<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/N<sub>2</sub>, CH<sub>4</sub>/N<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub>, and C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> separation.

Urea, as one of the most widely used nitrogen fertilizer, has the advantages of easy access and low price (Table S1), and was chosen as the SBU-tuning reagent for the micro-regulation of Cu-BTC channel. The objective of this work is to prepare a multifunctional adsorbent urea@Cu-BTC and investigate its performance in petrochemical separation. Experimental and computational approaches were combined to interpretate the origination of the enhanced adsorptive separation performance of urea@Cu-BTC in the potential application of refinery sweet dry gas separation. The urea@Cu-BTC adsorbent was thoroughly characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and N<sub>2</sub> sorption to provide structural information. Isotherms of key components in

refinery dry gas (including CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub>) were measured to derive thermodynamic properties of the adsorption processes. Dynamic breakthrough experiments were performed to estimate the performance of urea@Cu-BTC in potential petrochemical separation application. Based on the mechanism study, a strategy to prepare multifunctional petrochemical separation adsorbent was proposed to meet the ever-growing need of efficient separation processes in petroleum industry.

## 2. Experimental

## 2.1. Materials

Zinc oxide (ZnO, 99.99%, Aladdin); copper nitrate [Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, 99%, Damao Chemical Reagent Factory]; urea (99.9%, Guangzhou Chemical Reagent Factory); 1,3,5-Benzenetricarboxylic acid (H<sub>3</sub>BTC, 95%, J&K Scientific); N,Ndimethylformamide (DMF, AR) from Guangdong Guanghua Sci-Tech Co., Ltd. Ethanol and methanol from Damao Chemical Reagent Factory. All chemicals and reagents were used without further purification.

## 2.2. Synthesis

#### 2.2.1. Cu-BTC

ZnO (0.293 g) was dissolved in H<sub>2</sub>O (8 mL) under ultrasonication before adding DMF (16 mL). Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (1.74 g) was dissolved in H<sub>2</sub>O (8 mL) while H<sub>3</sub>BTC (0.84 g) was dissolved in EtOH (16 mL). All solutions were combined under stir to yield Cu-BTC crystallite as blue solid. The product was filtered and washed with DMF and

ethanol to remove the unreacted chemicals. Then, the solid was soaked in ethanol (12  $h \times 2$  times) and methanol (12  $h \times 2$  times) to evacuate DMF.

## 2.2.2. urea@Cu-BTC

The synthesis of urea@Cu-BTC was similar to that of Cu-BTC, except that a certain amount of urea was added to Cu(NO<sub>3</sub>)<sub>2</sub> aqueous solution with the urea/Cu molar ratio of 1:1, 1:3, 1:5. The corresponding products were labeled as urea<sub>1/1</sub>@Cu-BTC, urea<sub>1/3</sub>@Cu-BTC, urea<sub>1/5</sub>@Cu-BTC, respectively.

#### 2.3. Characterization

The scanning electron microscope (SEM) was conducted on Hitachi SU8220 to characterize the morphology of adsorbents. Samples were dispersed in EtOH by ultrasonication and then the supernatant was casted on aluminum foil attached with conductive glue. All samples were sputter coated with gold. Powder X-ray diffraction (PXRD) patterns were obtained on a Bruker D8 Advance diffractometer with Cu Kα radiation (40 mA, 40 kV) and at the scan speed of 2°/min. X-ray photoelectron spectroscopy (XPS) spectra was obtained with an Axis Ultra DLD instrument. N<sub>2</sub> isotherms were measured on a Micromeritics ASAP 2460 instrument at 77 K, where the surface area and pore volume were estimated with the built-in software.

#### 2.4. Isotherms

The samples were degassed at 393 K under vacuum for 6 hours before test. The isotherms of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub> were measured using a 3Flex

Surface Characterization Analyzer (Micromeritics, USA) at 288 K, 298 K, and 308 K.

## 2.5. Breakthrough curves

Breakthrough curves of equimolar CO<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> binary gas mixture were measured on the home-made breakthrough setup apparatus (Figure S1). Adsorbent (~ 0.5 g) was filled into a stainless-steel column (inner dimension  $5 \times 200$  mm) for each run. The gas mixture flowed through the column at the rate of 2 mL/min, and the eluent of the column was monitored with a gas chromatography (GC-9500, Shanghai Wuhao, China) equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID).

## 2.6. Molecular simulation

Molecular simulation was performed with Materials Studio 2017 software package for the mechanism investigation. DFT calculation was performed with Dmol<sup>3</sup> module<sup>[29]</sup> to calculate the binding energy in strong adsorption systems (i.e., chemisorption or adsorption on strongly polarized surface). All atoms were modeled using GGA/PW91 function and DNP+ basis set<sup>[30, 31]</sup>. Cu<sub>2</sub>BA<sub>4</sub> (BA = benzoic acid) was constructed to represent the SBU of Cu-BTC. Urea coordinated to Cu site with its nitrogen or via oxygen atom. Sorption module<sup>[32]</sup> was used to estimate adsorption energy at 100 kPa. All atoms are modeled with universal forcefield (UFF)<sup>[33]</sup> together with QEq method<sup>[34]</sup> to assign atomic partial charge. The Connolly surface method<sup>[35, 36]</sup> was used to calculate the porosity characteristics of Cu-BTC modified with varying ratios of urea. Hard spheres of CO<sub>2</sub> (3.3 Å) were used as probe molecules. Grid interval was set to 0.15 Å with the vdW scale factor of 1.00 Å. All structures were geometry optimized to their energy minimum. Binding energy was calculated following eqn(1):

$$E_{(binding \, energy)} = E_{(adsorbent+absorbent)} - E_{(adsorbent)} - E_{(absorbent)}$$
(1)

## 3. Results and Discussion

#### 3.1. Characterization

Figure 1(a) shows the N<sub>2</sub> isotherms of urea@Cu-BTCs and Cu-BTC at 77 K. All samples are of typical type-I isotherms, indicating predominant microporosity. Specific surface area and pore volume were calculated from N<sub>2</sub> isotherms and listed in Table 2. The presence of urea in Cu-BTC enhances its porosity, indicated by the significantly higher specific surface area and pore volume of urea@Cu-BTCs. More importantly, the ultra-micro porosity (<7 Å) is enhanced with the increase in urea amount. Besides, urea grafting also creates enhanced confinement in the microporosity of urea@Cu-BTC, implied by the shift of pore size distribution from 9.6 Å (Cu-BTC) to 7.3 Å (urea<sub>1/5</sub>@Cu-BTC) to 6.8 Å (urea<sub>1/3</sub>@Cu-BTC) to 5.9 Å (urea<sub>1/1</sub>@Cu-BTC) as is shown in Figure 1(b). Such phenomena would only happen when: (1) the presence of urea does not compromise the growth of Cu-BTC crystal; (2) the introduced urea coordinates to Cu sites to enable monomolecular dispersion. The former precondition could be evidenced by XRD (Figure S2) and SEM (Figure S3), where all characteristic diffraction peaks of Cu-BTC are preserved in the case of urea@Cu-BTC, and urea@Cu-BTC preserves the octahedral shape of Cu-BTC crystal but with more pronounced defects. The later precondition is supported by XPS (Figure S4), where the binding energy of Cu 2p<sub>3/2</sub> shifts from 933.43 eV of Cu-BTC to 932.06 eV of urea<sub>1/3</sub>@Cu-BTC with a chemical shift of -1.37 eV, indicating the decrease in Cu oxidation state caused by the coordination of urea. On the other hand, the presence of urea brings in distortion and defect to Cu-BTC crystals. As a result, the specific surface area first increases and then decreases with the increase in urea amount. Therefore, urea<sub>1/3</sub>@Cu-BTC exhibits the highest specific surface area and pore volume among all urea@Cu-BTCs. Hence the label urea@Cu-BTC is used to represent urea<sub>1/3</sub>@Cu-BTC in the following discussion for the sake of conciseness.



Figure 1 (a)  $N_2$  isotherms and (b) pore-size distribution of urea@Cu-BTCs and Cu-BTC

Adsorbents	Surface area (m <sup>2</sup> g <sup>-1</sup> )		Pore volume (cm <sup>3</sup> g <sup>-1</sup> )			
Ausorbents	BET	Langmuir	V <sub>total</sub>	V <sub>micro</sub>	V <sub>meso</sub>	
urea <sub>1/1</sub> @Cu-BTC	1746	2132	0.71	0.60	0.11	
urea <sub>1/3</sub> @Cu-BTC	1901	2182	0.79	0.65	0.14	
urea <sub>1/5</sub> @Cu-BTC	1829	2055	0.74	0.63	0.11	
Cu-BTC	1462	1689	0.63	0.50	0.13	

Table 2 Porosity parameters of Cu-BTC and urea@Cu-BTCs.

#### 3.2. Adsorptive Separation

#### 3.2.1. CO<sub>2</sub> Stripping

Since  $CH_4$  (31.38%) and  $N_2$  (20.40%) are the major components in refinery dry gas as shown in Table 1, the major challenges in CO<sub>2</sub> stripping are the selective separation of CO<sub>2</sub> from N<sub>2</sub> and CH<sub>4</sub> under moisture. Figure 2(a) compares the isotherms of CO<sub>2</sub>, CH<sub>4</sub> and N2 on urea@Cu-BTC and Cu-BTC at 298 K. The adsorptive capacity of urea@Cu-BTC for CO<sub>2</sub>, CH<sub>4</sub> reaches 5.9 mmol/g, 1.1 mmol/g at 298 K and 1 bar, being 23.7% and 10.2% higher that of Cu-BTC, respectively. Isosteric heat of adsorption (Qst) is calculated (Table S2-3) using the Virial equation (S1) derived from the adsorption isotherms of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> at 288 K, 298 K and 308 K (Figure S6-7). Figure 2(b) exhibits the isosteric heat of CO<sub>2</sub> (27.8 kJ/mol), CH<sub>4</sub> (18.5 kJ/mol) and N<sub>2</sub> (14.9 kJ/mol) adsorption on urea@Cu-BTC at zero coverage surpasses that on Cu-BTC, indicating higher affinity of urea@Cu-BTC towards CO<sub>2</sub>/CH<sub>4</sub>/N<sub>2</sub> adsorption. The slight increase in CH<sub>4</sub> and N<sub>2</sub> affinity could be attributed to the enhanced confinement of urea@Cu-BTC channels resulted from the presence of urea. Moreover, the substantially higher isosteric heat of CO<sub>2</sub> adsorption on urea@CuBTC than that of CH<sub>4</sub> and N<sub>2</sub> indicates the promising potential of its selective adsorption of CO<sub>2</sub> from refinery dry gas. The adsorptive selectivity of CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> equimolar mixtures is evaluated using ideal adsorbed solution theory (IAST, S2). Single-component isotherms of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> are fitted by the dual sites Langmuir-Freundlich model (Table S4-5), and then the adsorptive selectivity of binary mixture is defined in eqn(2):

$$S_{1,2} = \frac{x_1/x_2}{y_1/y_2}$$
 (2)

where  $x_1$  and  $x_2$  represent the molar fractions of components 1 and 2 in the adsorbed phase, while  $y_1$  and  $y_2$  represent that in the gas phase. As a result, the IAST selectivity of equimolar CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> on urea@Cu-BTC reaches 9.5 and 95.2 (Figure 2c), being 19.8% and 59.9% higher than that on Cu-BTC, respectively.

Figure 2(d-f) compare the DFT-optimized configuration of CO<sub>2</sub> adsorption on urea@Cu-BTC and Cu-BTC to interpret the origination of the enhanced CO<sub>2</sub> selectivity. Urea coordinates to Cu sites by its nitrogen atom (Figure 2d, 39.4 kJ/mol) or oxygen atom (Figure 2e, 37.0 kJ/mol). Either way, CO<sub>2</sub> adsorption was uncompromised when compared to that of Cu-BTC (Figure 2f, 26.4 kJ/mol). It is plausible that the presence of urea introduces new adsorption sites that strongly adsorb CO<sub>2</sub> under the synergy of polarization from N/O and the enhanced confinement effect, leading to the improved CO<sub>2</sub> stripping performance of urea@Cu-BTC (Figure S5).



Figure 2 (a) Isotherms, (b) isosteric heat of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> adsorption, (c) IAST selectivity of equimolar  $CO_2/N_2$  and  $CO_2/CH_4$  on urea@Cu-BTC and Cu-BTC, and

DFT-optimized configuration and binding energy of CO<sub>2</sub> adsorption on (d, e) urea@Cu-BTC, (f) Cu-BTC.

## 3.2.2. C<sub>3</sub>H<sub>6</sub> Recovery

After CO<sub>2</sub> stripping in column A, C2 and C3 hydrocarbons are recovered and separated from column B (Scheme 1). Column C separates C3 (Table S6) to produce polymergrade propylene, where key requirement to adsorbents is the selective recovery of C<sub>3</sub>H<sub>6</sub> (86.54%) from  $C_3H_8$  (13.46%). Figure 3(a) compares isotherms of  $C_3H_6$  and  $C_3H_8$  on urea@Cu-BTC and Cu-BTC at 298 K, where the C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> uptakes of urea@Cu-BTC are 9.4 mmol/g and 8.3 mmol/g at 298 K and 1 bar, being 8.8% and 12.2% higher than that on Cu-BTC. Figure 3(b) suggests that  $Q_{st}$  of  $C_3H_6$  adsorption is higher than C<sub>3</sub>H<sub>8</sub> on both adsorbents, except that urea@Cu-BTC exhibits 24.6% higher isosteric heat of C<sub>3</sub>H<sub>6</sub> adsorption (41.0 kJ/mol) than that on Cu-BTC (32.9 kJ/mol). Figure 3(c) shows that the energy distribution of the adsorbed C<sub>3</sub>H<sub>6</sub> molecules exhibits three peaks on Cu-BTC, corresponding to the strongest unsaturated Cu site ( $\pi$ -complexation, -94.4 kJ/mol), the tetrahedral pocket site (3.5 Å, -74.4 kJ/mol), and the channel site (9 Å, -59.4 kJ/mol)<sup>[23]</sup>. For the case of urea@Cu-BTC, only two peaks are observed. The peak representing  $\pi$ -complexation disappears due to the steric hinderance of urea, which results in lower probability of accessible Cu site. However, the presence of urea brings in new adsorption site at -81.3 kJ/mol, which is enhanced by 9.3% than the original pocket sites, accounting for the 6.7% improved C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> selectivity as shown in Figure 3(d). Figure S8 and Table S9 indicate that the increase in urea amount imposes stronger confinement on the porosity of urea@Cu-BTC, facilitating the formation of



the new-creating strong sites for C<sub>3</sub>H<sub>6</sub> selective adsorption.

Figure 3 (a) Isotherms, (b) isosteric heat of  $C_3H_6$  and  $C_3H_8$  adsorption, (c) simulated interaction energy, (d) IAST selectivity of equimolar  $C_3H_6/C_3H_8$  on urea@Cu-BTC and Cu-BTC.

## 3.3.3. C<sub>2</sub>H<sub>4</sub> Recovery

Column D separates C2 to produce polymer-grade ethylene (Table S7), where the key process is to recover C<sub>2</sub>H<sub>4</sub> (52.35%) from C<sub>2</sub>H<sub>6</sub> (47.65%). Figure 4(a) compares the isotherms of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> on urea@Cu-BTC and Cu-BTC. The adsorption capacities of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> on urea@Cu-BTC are 7.9 mmol/g and 6.6 mmol/g at 298 K and 1 bar, respectively, being 10.9% and 9.2% higher than that on Cu-BTC. Figure 4(b) shows that the isosteric heat of C<sub>2</sub>H<sub>4</sub> on urea@Cu-BTC at zero coverage (38.3 kJ/mol) is 10.2% higher than that on Cu-BTC, which results in the improved adsorptive separation performance. Figure 4(c) indicates the presence of new adsorption sites in urea@Cu-





Figure 4 (a) Isotherms, (b) isosteric heat of  $C_2H_4$  and  $C_2H_6$  adsorption, (c) simulated interaction energy, (d) IAST selectivity of equimolar  $C_2H_4/C_2H_6$  on urea@Cu-BTC and Cu-BTC.

## 3.3.4. CH<sub>4</sub> Recovery

After C2 and C3 separation, CH<sub>4</sub> is recovered from column E (Table S8) where the main challenge is the efficient extraction of CH<sub>4</sub> (47.84%) from N<sub>2</sub> (31.10%). Urea@Cu-BTC adsorbs 10.2% more CH<sub>4</sub> (1.1 mmol/g) than Cu-BTC at ambient conditions (Figure 5a), together with the 22.6% and 19.4% enhanced isosteric heat of CH<sub>4</sub> (18.5 kJ/mol) and N<sub>2</sub> (14.9 kJ/mol) adsorption (Figure 5b). There are two major peaks for CH<sub>4</sub> adsorption on urea@Cu-BTC (Figure 5c), representing the channel site (-15.9 kJ/mol) and the tetrahedral pocket site (-28.2 kJ/mol), being 11.6% and 3.3%

higher than that on Cu-BTC. As a result, urea@Cu-BTC has a 15.2% increased  $CH_4/N_2$ 

selectivity (Figure 5d).



Figure 5 (a) Isotherms, (b) isosteric heat of  $CH_4$  and  $N_2$  adsorption, (c) simulated interaction energy, (d) IAST selectivity of equimolar  $CH_4/N_2$  on urea@Cu-BTC and Cu-BTC.

## 3.4. Comprehensive Assessment

## 3.4.1. Adsorption Equilibrium

The capacity of urea@Cu-BTC toward all the major hydrocarbons in refinery dry gas has been improved when compared to that of Cu-BTC (Figure 6a), which could be ascribed to the increased isosteric heat of adsorption (Figure 6b). Figure 7 compares the isosteric heat of adsorption and capacity of urea@Cu-BTC with other reported MOFs<sup>[37-48]</sup>, where urea@Cu-BTC exhibits moderate isosteric heat of C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, and CO<sub>2</sub> adsorption but superior capacity at ambient conditions (Table S10-13 for additional data). The main competitor to urea@Cu-BTC is Mg-MOF-74<sup>[49, 50]</sup>, who can utilize its abundant unsaturated metal sites to strongly adsorb olefins *via*  $\pi$ -complexation and CO<sub>2</sub> through its quadrupole moment. On the contrary, urea@Cu-BTC holds the advantage of more feasible regeneration due to lower isosteric heat of adsorption.



Figure 6 (a) The adsorption amount (b) the  $Q_{st}$  of  $C_3H_6$ ,  $C_3H_8$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $CO_2$ ,  $CH_4$  and  $N_2$  on urea@Cu-BTC and Cu-BTC at 298 K and 1 bar.



Figure 7 A comparison of urea@Cu-BTC and the reported materials in aspect of

isosteric heat and (a) C<sub>3</sub>H<sub>6</sub> uptake (b) C<sub>2</sub>H<sub>4</sub> uptake (c) CO<sub>2</sub> uptake (d) CH<sub>4</sub> uptake.

## 3.4.2. Moisture Stability

CO<sub>2</sub> was used as the molecular probe to estimate the moisture stability of urea@Cu-BTC. Figure 8(a) shows a drastic loss of 91% in CO<sub>2</sub> capacity for Cu-BTC under RH= 55% moisture for 20 days. On the contrary, urea@Cu-BTC experienced a slight loss of 11% under the same conditions. Figure 8(b) suggests that the crystal structure of Cu-BTC collapses on the 7<sup>th</sup> day while the crystal structure of urea@Cu-BTC remains after 20 days. DFT calculation indicates that urea coordinates to Cu-BTC via its oxygen atom (Figure 9a) or its nitrogen atom (Figure 9b), and their exothermal binding energies are calculated to be 93.6 kJ/mol and 98.6 kJ/mol, respectively, which are much stronger than the binding energy between H<sub>2</sub>O and Cu-BTC (Figure 9c, 59.8 kJ/mol). Therefore, the coordinate of urea protects Cu site from H<sub>2</sub>O attack under moisture.



**Figure 8** (a) CO<sub>2</sub> uptake (b) XRD of urea@Cu-BTC and Cu-BTC after the exposure to 55% humidity in air at 298 K.



Figure 9 DFT optimized SBU microenvironments for the models of interest

## 3.5. Dynamic Breakthrough Experiment

The dynamic breakthrough curves in Figure 10 shows that the challenging separation of CO<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> mixtures can be achieved with the column filled with urea@Cu-BTC at room temperature. Besides, urea@Cu-BTC possesses higher working capacity indicated by its longer retention time. The retention time of CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> on urea@Cu-BTC is 36.9%, 61.7%, 26.0% and 17.2% longer than that on Cu-BTC. Moreover, urea@Cu-BTC exhibits enhanced separation performance than that of Cu-BTC, indicated by the more conspicuous difference between retention time of two components. The ratio of CO<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> retention time difference of urea@Cu-BTC are enhanced by 36.1%, 61.7%, 33.9% and 23.7% when compared with that of Cu-BTC. Hence, micro-regulating the channel of MOFs is a feasible strategy for petrochemical adsorbents.



Figure 10 The dynamic breakthrough curve of (a)  $CO_2/CH_4$  (b)  $CO_2/N_2$  (c)  $C_2H_6/C_2H_4$ and (d)  $C_3H_8/C_3H_6$  through fixed bed packed with urea@Cu-BTC and Cu-BTC at 298 K and 1 bar.

## 4. Conclusions

In conclusion, multifunctional adsorbents urea@Cu-BTCs were prepared from cheap building blocks at room temperature yet exhibiting generally enhanced adsorptive separation performance. The CO<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and CH<sub>4</sub> uptakes on urea@Cu-BTC were up to 5.9 mmol/g, 9.4 mmol/g, 7.9 mmol/g and 1.1 mmol/g and the corresponding adsorptive selectivity of CO<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/N<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>, and CH<sub>4</sub>/N<sub>2</sub> on urea@Cu-BTC improved 19.8%, 59.9%, 6.7%, 8.7%, and 15.2% than that on Cu-BTC, respectively. Besides, the moisture stability of urea@Cu-BTC was significantly enhanced. Molecular simulation interpreted the mechanism of the improved adsorptive separation performance, and attributed it to the enhanced confinement effect brought by micro-regulating the channel with urea. Besides, the enhanced moisture stability was ascribed to the coordination of urea, which protects Cu site from H<sub>2</sub>O attack under moisture. Furthermore, the major components of refinery dry gas could be well separated using a column filled with urea@Cu-BTC, demonstrating micro-regulating the channel of MOFs provides a feasible strategy for the fabrication of advanced petrochemical adsorbents.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## References

- Liu, Q.,Jin, Z.,Wang, X.,Yi, J.,Meng, Q.,Wu, X.,Gao, B.,Nie, H.,Zhu, D. Distinguishing kerogen and oil cracked shale gas using H, C-isotopic fractionation of alkane gases[J]. *Marine and Petroleum Geology*, 2018, 91, 350-362.
- [2] Zhao, M. Application of shallow cold oil absorption technology in recovery of refinery dry gas[J]. *Modern Chemical Industry*, 2022, 42 (9).
- [3] Wang, Y., Peh, S. B., Zhao, D. Alternatives to Cryogenic Distillation: Advanced Porous Materials in Adsorptive Light Olefin/Paraffin Separations[J]. *Small*, 2019, 15 (25), e1900058.
- [4] Sholl, D. S., Lively, R. P. Seven chemical separations to change the world[J].*Nature*, **2016**, *532(7600)* (435).
- [5] Fakhraei Ghazvini, M., Vahedi, M., Najafi Nobar, S., Sabouri, F. Investigation of the MOF adsorbents and the gas adsorptive separation mechanisms[J]. *Journal* of Environmental Chemical Engineering, 2021, 9 (1).
- Jiang, C., Wang, X., Ouyang, Y., Lu, K., Jiang, W., Xu, H., Wei, X., Wang, Z., Dai,
  F., Sun, D. Recent advances in metal–organic frameworks for gas adsorption/separation[J]. *Nanoscale Advances*, 2022, 4 (9), 2077-2089.
- [7] Li, X.,Bian, H.,Huang, W.,Yan, B.,Wang, X.,Zhu, B. A review on anion-pillared metal–organic frameworks (APMOFs) and their composites with the balance of adsorption capacity and separation selectivity for efficient gas separation[J]. *Coordination Chemistry Reviews*, 2022, 470.

- [8] Liu, P., Wang, Y., Chen, Y., Wang, X., Yang, J., Li, L., Li, J. Stable titanium metalorganic framework with strong binding affinity for ethane removal[J]. *Chinese Journal of Chemical Engineering*, 2022, 42, 35-41.
- [9] Li, J. R., Kuppler, R. J., Zhou, H. C. Selective gas adsorption and separation in metal-organic frameworks[J]. *Chem Soc Rev*, 2009, 38 (5), 1477-504.
- [10] Liu, Y.,Wu, Y.,Liang, W.,Peng, J.,Li, Z.,Wang, H.,Janik, M. J.,Xiao, J. Bimetallic ions regulate pore size and chemistry of zeolites for selective adsorption of ethylene from ethane[J]. *Chemical Engineering Science*, 2020, 220.
- [11] Kulawong, S., Artkla, R., Sriprapakhan, P., Maneechot, P. Biogas purification by adsorption of hydrogen sulphide on NaX and Ag-exchanged NaX zeolites[J]. *Biomass and Bioenergy*, 2022, 159.
- [12] Zhou, X.,Miao, G.,Xu, G.,Luo, J.,Yang, C.,Xiao, J. Mixed (Ag<sup>+</sup>, Ca<sup>2+</sup>)-LTA zeolite with suitable pore feature for effective separation of C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub>[J].
  *Chemical Engineering Journal*, 2022, 450.
- [13] Du, S., Wang, X., Huang, J., Kent, K., Huang, B., Karam, I., Li, Z., Xiao, J. Ultramicroporous carbons featuring sub-Ångstrom tunable apertures for the selective separation of light hydrocarbon[J]. *AIChE Journal*, **2021**, *67* (9).
- [14] Geng, J.-C.,Xue, D.-M.,Liu, X.-Q.,Shi, Y.-Q.,Sun, L.-B. N-doped porous carbons for CO2capture: Rational choice of N-containing polymer with high phenyl density as precursor[J]. *AIChE Journal*, **2017**, *63* (5), 1648-1658.
- [15] Yang, R. T., Kikkinides, E. S. New Sorbents for Olefinparaffin Separations by

Adsorption via  $\pi$ -Complexation[J]. *AIChE Journal*, **1995**, *41* (3), 509–517.

- [16] Wang, G.-D., Chen, J., Li, Y.-Z., Hou, L., Wang, Y.-Y., Zhu, Z. A robust ethaneselective metal-organic framework with nonpolar pore surface for efficient C<sub>2</sub>H<sub>6</sub>/C<sub>2</sub>H<sub>4</sub> separation[J]. *Chemical Engineering Journal*, **2021**, *433* (133786).
- [17] Zeng, Z., Wang, W., Xiong, X., Zhu, N., Xiong, Y., Wei, Z., Jiang, J. J. Flexible Microporous Copper(II) Metal-Organic Framework toward the Storage and Separation of C1-C3 Hydrocarbons in Natural Gas[J]. *Inorg Chem*, 2021, 60 (12), 8456-8460.
- [18] Hong, A. N., Yang, H., Li, T., Wang, Y., Wang, Y., Jia, X., Zhou, A., Kusumoputro, E., Li, J., Bu, X., Feng, P. Pore-Space Partition and Optimization for Propane-Selective High-Performance Propane/Propylene Separation[J]. ACS Appl Mater Interfaces, 2021, 13, 52160-52166.
- [19] Xu, F.,Xian, S. K.,Xia, Q. B.,Li, Y. W.,Li, Z. Effect of Textural Properties on the Adsorption and Desorption of Toluene on the Metal-Organic Frameworks HKUST-1 and MIL-101[J]. *Adsorption Science & Technology*, 2013, 31 (4), 325-339.
- [20] Zhao, Z., Wang, S., Yang, Y., Li, X., Li, J., Li, Z. Competitive adsorption and selectivity of benzene and water vapor on the microporous metal organic frameworks (HKUST-1)[J]. *Chemical Engineering Journal*, 2015, 259, 79-89.
- [21] Martins, V. F. D., Ribeiro, A. M., Ferreira, A., Lee, U. H., Hwang, Y. K., Chang, J.-S., Loureiro, J. M., Rodrigues, A. E. Ethane/ethylene separation on a copper benzene-1,3,5-tricarboxylate MOF[J]. Separation and Purification Technology,

**2015**, *149*, 445-456.

- [22] Najafi Nobar, S., Farooq, S. Experimental and modeling study of adsorption and diffusion of gases in Cu-BTC[J]. *Chemical Engineering Science*, 2012, 84, 801-813.
- [23] Vishnyakov, A., Ravikovitch, P. I., Neimark, A. V., Bülow, M., Wang, Q. M. Nanopore Structure and Sorption Properties of Cu–BTC Metal–Organic Framework[J]. *Nano Letters*, 2003, 3 (6), 713–718.
- [24] Decoste, J. B., Peterson, G. W., Smith, M. W., Stone, C. A., Willis, C. R. Enhanced stability of Cu-BTC MOF via perfluorohexane plasma-enhanced chemical vapor deposition[J]. *J Am Chem Soc*, **2012**, *134* (3), 1486-9.
- [25] Xu, S.,Guo, X.,Qiao, Z.,Huang, H.,Zhong, C. Methyl-Shield Cu-BTC with High Water Stability through One-Step Synthesis and In Situ Functionalization[J]. *Industrial & Engineering Chemistry Research*, 2020, 59 (27), 12451-12457.
- [26] Li, H.,Lin, Z.,Zhou, X.,Wang, X.,Li, Y.,Wang, H.,Li, Z. Ultrafast room temperature synthesis of novel composites Imi@Cu-BTC with improved stability against moisture[J]. *Chemical Engineering Journal*, 2017, 307, 537-543.
- [27] Lin, Z., Lv, Z., Zhou, X., Xiao, H., Wu, J., Li, Z. Postsynthetic Strategy To Prepare ACN@Cu-BTCs with Enhanced Water Vapor Stability and CO<sub>2</sub>/CH<sub>4</sub> Separation Selectivity[J]. *Industrial & Engineering Chemistry Research*, 2018, 57 (10), 3765-3772.

- [28] Wu, Y.,Lv, Z.,Zhou, X.,Peng, J.,Tang, Y.,Li, Z. Tuning secondary building unit of Cu-BTC to simultaneously enhance its CO<sub>2</sub> selective adsorption and stability under moisture[J]. *Chemical Engineering Journal*, **2019**, *355*, 815-821.
- [29] Dance, I. Evaluations of the accuracies of DMol3 density functionals for calculations of experimental binding enthalpies of N<sub>2</sub>, CO, H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub> at catalytic metal sites[J]. *Molecular Simulation*, **2017**, *44* (7), 568-581.
- [30] Handzlik, J.,Kurleto, K. Assessment of density functional methods for thermochemistry of chromium oxo compounds and their application in a study of chromia–silica system[J]. *Chemical Physics Letters*, **2013**, *561-562*, 87-91.
- [31] Grimme, S., Antony, J., Ehrlich, S., Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu[J]. *J Chem Phys*, **2010**, *132* (15), 154104.
- [32] Akkermans, R. L. C., Spenley, N. A., Robertson, S. H. Monte Carlo methods in Materials Studio[J]. *Molecular Simulation*, 2013, 39 (14-15), 1153-1164.
- [33] Rappe, A. K., Casewit, C. J., Colwell, K. S., III, W. A. G., Skiff, W. M. UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations[J]. *Journal of the American Chemical Society*, **1992**, *114* (25), 10024–10035.
- [34] Wilmer, C. E.,Kim, K. C.,Snurr, R. Q. An Extended Charge Equilibration Method[J]. J Phys Chem Lett, 2012, 3 (17), 2506-11.
- [35] Cao, J., Pham, D. K., Tonge, L., Nicolau, D. V. Study of atomic force microscopy force-distancecurves by simulation using the Connolly surfacefor proteins[J].

Smart Materials and Structures, 2002, 11 (767).

- [36] Cao, J., Pham, D. K., Tonge, L., Nicolau, D. V. Predicting surface properties of proteins on the Connolly molecular surface[J]. *Smart Materials and Structures*, 2002, 11 (772).
- [37] Lin, R. B.,Li, L.,Zhou, H. L.,Wu, H.,He, C.,Li, S.,Krishna, R.,Li, J.,Zhou,
  W.,Chen, B. Molecular sieving of ethylene from ethane using a rigid metalorganic framework[J]. *Nat Mater*, 2018, *17* (12), 1128-1133.
- Bloch, E. D., Queen, W. L., Krishna, R., Zadrozny, J. M., Brown, C. M., Long, J.
  R. Hydrocarbon Separations in a Metal-Organic Framework with Open Iron(II)
  Coordination Sites[J]. *Science*, 2012, 335 (6076), 1606-1610.
- [39] Yang, S.,Ramirez-Cuesta, A. J.,Newby, R.,Garcia-Sakai, V.,Manuel, P.,Callear, S. K.,Campbell, S. I.,Tang, C. C.,Schroder, M. Supramolecular binding and separation of hydrocarbons within a functionalized porous metal-organic framework[J]. *Nat Chem*, **2014**, 7 (2), 121-9.
- [40] Bae, Y. S., Lee, C. Y., Kim, K. C., Farha, O. K., Nickias, P., Hupp, J. T., Nguyen, S. T., Snurr, R. Q. High propene/propane selectivity in isostructural metal-organic frameworks with high densities of open metal sites[J]. *Angew Chem Int Ed Engl*, 2012, *51* (8), 1857-60.
- [41] Chen, Y., Tu, S., Fu, P., Wu, H., Wang, X., Wu, Y., Li, Z., Xia, Q. A cobalt-based metal–organic framework for efficient separation of propene from propane via electrostatic effect[J]. *AIChE Journal*, **2022**, *68* (8).
- [42] Wu, H., Yuan, Y., Chen, Y., Xu, F., Lv, D., Wu, Y., Li, Z., Xia, Q. Efficient

adsorptive separation of propene over propane through a pillar-layer cobaltbased metal–organic framework[J]. *AIChE Journal*, **2019**, *66* (4), e16858.

- [43] Pirzadeh, K.,Esfandiari, K.,Ghoreyshi, A. A.,Rahimnejad, M. CO<sub>2</sub> and N<sub>2</sub> adsorption and separation using aminated UiO-66 and Cu<sub>3</sub>(BTC)<sub>2</sub>: A comparative study[J]. *Korean Journal of Chemical Engineering*, **2020**, *37* (3), 513-524.
- [44] Lin, J.-B., Nguyen, T. T. T., Vaidhyanathan, R., Burner, J., Taylor, J. M., Durekova, H., Akhtar, F., Mah, R. K., Ghaffari-Nik, O., Marx, S., Fylstra, N., Iremonger, S. S., Dawson, K. W., Sarkar, P., Hovington, P., Rajendran, A., Woo, T. K., Shimizu, G. K. H. A scalable metal-organic framework as a durable physisorbent for carbon dioxide capture[J]. *science*, 2021, *374*, 1464-1469.
- [45] Maity, R.,Singh, H. D.,Yadav, A. K.,Chakraborty, D.,Vaidhyanathan, R. Waterstable Adenine-based MOFs with Polar Pores for Selective CO<sub>2</sub> Capture[J]. *Chem Asian J*, **2019**, *14* (20), 3736-3741.
- [46] Liu, X.-W.,Gu, Y.-M.,Sun, T.-J.,Guo, Y.,Wei, X.-L.,Zhao, S.-S.,Wang, S.-D.
  Water Resistant and Flexible MOF Materials for Highly Efficient Separation of Methane from Nitrogen[J]. *Industrial & Engineering Chemistry Research*, 2019, 58 (44), 20392-20400.
- [47] Lv, D., Wu, Y., Chen, J., Tu, Y., Yuan, Y., Wu, H., Chen, Y., Liu, B., Xi, H., Li, Z., Xia,
  Q. Improving CH<sub>4</sub>/N<sub>2</sub> selectivity within isomeric Al-based MOFs for the highly selective capture of coal-mine methane[J]. *AIChE Journal*, 2020, 66 (9), e16287.
- [48] Shekhah, O.,Belmabkhout, Y.,Chen, Z.,Guillerm, V.,Cairns, A.,Adil,

K.,Eddaoudi, M. Made-to-order metal-organic frameworks for trace carbon dioxide removal and air capture[J]. *Nat Commun,* **2014**, *5*, 4228.

- [49] He, Y.,Krishna, R.,Chen, B. Metal–organic frameworks with potential for energy-efficient adsorptive separation of light hydrocarbons[J]. *Energy & Environmental Science*, 2012, 5, 9107-9120.
- [50] Yang, D.-A.,Cho, H.-Y.,Kim, J.,Yang, S.-T.,Ahn, W.-S. CO<sub>2</sub> capture and conversion using Mg-MOF-74 prepared by a sonochemical method[J]. *Energy Environ. Sci.*, 2012, 5 (4), 6465-6473.