Carbamate-isocyanurate-bridged periodic mesoporous organosilica for van der Waals CO₂ capture

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Content	Page
Title Page	S1
Synthesis Schemes of THEIC Organosiloxane Bridge	S2
Structural Characterization of THEIC Bridge	S3
Materials Characterization	S7
CO ₂ Tests Results	S 8
Density Functional Calculations	S10
Experimental Section	S12
Reference	S13

1. Synthesis Schemes of THEIC Organosiloxane Bridge

Synthesis of THEIC bridge was performed by the solvent-free reaction of 1,3,5-tris(2-hydroxythyl)isocyanurate (THEIC) with 3-(triethoxysilyl)propyl silane (IPTES) at melting temperature of THEIC (**Scheme S1**). This led to the synthesis of a new organosiloxane compound, which were characterized and identified by ¹H-NMR, ¹³C-NMR (**Figure S1**), and mass spectroscopy (**Figure S2**). Synthesis of PMO-THEIC was achieved through a triblock copolymer, P123, as a soft template in acidic conditions in which the THEIC bridge and TEOS are hydrolyzing and co-condensing to form a sol-gel in the solution at 40 °C. The aging at 100 °C and subsequent treatment with MeOH led to the removal of the template (P123) from the pore channels.



Scheme S1. Schematic illustration of THEIC organosiloxane bridge synthesis and the mechanism of PMO-THEIC formation in brief.

2. Structural Characterization of THEIC Bridge

Physical and spectral data of 1,3,5-tris(2-(3-(triethoxysilyl)propoxy)ethyl)-1,3,5-triazinane-2,4,6-trione (THEIC bridge): Colorless liquid. ¹H-NMR (300 MHz, DMSO-d₆): δ 0.60 (t, *J* = 8.1 Hz, CH₂), 1.22 (m, CH₃), 1.61 (m, CH₂), 3.11 (m, CH₂), 3.80 (q, *J* = 6.9 Hz, CH₂), 4.16 (m, CH₂), 4.28 (m, CH₂), 5.18 (s, NH). ¹³C-NMR (75 MHz, DMSO-d₆): δ 7.55, 18.26, 23.25, 43.41, 46.50, 58.40, 61.05, 148.94, 156.23. MS (70 eV) *m/z* 716 (M⁺), 670, 541, 469, 294, 248

Electronic Supplementary Information



Figure S1. ¹³C-NMR spectra of THEIC bridge.



Figure S2. ¹H-NMR spectra of THEIC bridge.



Figure S3. Mass spectrum of THEIC bridge.

Next, three different ratios of THEIC to TEOS (*i.e.*, 1:3, 1:9, and 1:15, respectively) were used for the synthesis of PMO-THEIC. Then, the surface area for each obtained PMO was carefully examined. Accordingly, the molar ratio of 1:15 led to the highest surface area (697 m².g⁻¹) when compared to other ratios (**Figure S4**).



Figure S4. N₂ adsorption-desorption isotherms of PMO-THEIC with three different molar ratios of THEIC bridge to TEOS, including 1:3, 1:9, and 1:15, respectively.



Figure S5. Low magnification SEM image of PMO-THEIC.



Figure S6. TG-DTA analysis of PMO-THEIC.

3. Materials Characterization

TG-DTA analysis of PMO-THEIC was recorded using a Rigaku Thermo plus TG8120 apparatus. XRD pattern was collected by a Rigaku X-ray diffractometer with Cu Kα radiation at 30 KV and 15 mA. Fourier-transform infrared spectroscopy (FTIR) spectra were recorded on a Shimadzu FTIR-4200. The SEM images were observed with a HITACHI SU-8230 scanning SEM. TEM images were taken with a JEOL JEM-2100F microscope (operated at 300 kV). N₂ adsorption/desorption and BJH analyses were carried out at –196 °C using a Microtrac Bel BEL-mini. Before the measurements, the sample was evacuated at 90 °C for 20-24 h. CO₂ adsorption analyses were recorded by MicroActive for TriStar II Plus 2.03. ¹H-NMR and ¹³C-NMR spectra were recorded by JEOL Delta 75 and 300 MHz spectrometers, respectively. ²⁹Si magic-angle spinning (MAS) NMR spectra and ¹³C cross-polarized (CP) MAS NMR spectra were recorded at 119.17 MHz on a Varian 600PS solid-state NMR spectrometer using a 6 mm diameter zirconia rotor.

4. CO₂ Tests Results

The comparative results indicate that PMO-THEIC has \sim 3 folds higher CO₂ capture capacity compared to SBA-15, which reveals that CO₂ capture capacity has been enhanced three times once the bridge is embedded in the pore walls. Furthermore, the previously reported PMOs were compared with PMO-THEIC in Table S1. Although urea-bridged PMO, which also has a pyridine group in each molecule of the bridge, CO₂ capture capacity is lower than that of PMO-THEIC. The only case in which its capacity is observed to be higher than that PMO-THEIC is a PMO that is post-modified with amine groups. This higher activity is because of the high tendency of amine group toward CO₂ capture. However, the amine group is not stable in air and maybe oxidized in long term exposure to air oxygen.

Entry	Adsorbent	BET surface area (m ² g ⁻¹)	CO ₂ adsorption (mmol/g)	Remarks	Ref.
1	PMO-UDF-15	979	0.62	The bridge has two urea sites with one pyridine core.	14
2	BPMO	645	0.57	The bridge is a benzene.	15
3	A2-BPMO	180	3.03	The PMO here is postmodified with an amine group	15
5	PMO-DADD	450	0.88	Every mole of bridge here has four amine functions with a long aliphatic chain	16
6	SBA-15	650	0.4	This silica mesopore has no functional group is as reference sample	This work
4	PMO-THEIC *	697	1.1	it contains three carbamate groups in each bridge which is linked with isocyanurate core	This work

Table S1. Comparison of previously published mesoporous materials with PMO-THEIC at 25 °C.

The heat of adsorption (Q_{st}) values were obtained for PMO-THEIC according to the adsorbed CO_2 values obtained at two different temperatures (273 K and 298 K) and the Q_{st} was depicted as a function of the amounts of adsorbed CO_2 into PMO-THEIC. The values of Q_{st} were obtained according to the standard method using the following equation:

$$\ln\left(\frac{P1}{P2}\right) = \frac{Q_{st}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$



Figure S7. Heat of adsorption plot (Q_{st}) for CO₂ capture test in PMO-THEIC for different the amount of adsorbed CO₂ at 273 K and 298 K.





5. Density Functional Calculations

Gamma-point density functional calculations were carried out within the framework of the projector augmented wave formalism¹ with Perdew-Burke-Ernzerhof functional for general gradient approximation (GGA)^{2, 3} as implemented in the VASP code.⁴ The van der Waals interaction was taken into account based on Klimeš formalism.^{5, 6} Since the DFT study was aimed at understanding the interaction between CO₂ and THEIC bridge, we first optimized the THEIC structure capped with Si(OH)₃ at each end to forces smaller than 0.05 Å⁻¹. The THEIC structure was placed in a large box of 30 Å × 30 Å × 30 Å, shown in the inset of Figure S9, to prevent THEIC structure from interacting with its own image created by the periodic boundary conditions.

Capping large molecular units with H, as employed here, has been proven the to be effective for economically simulating large molecules and structures.^{7, 8}

We then examined the interaction between CO_2 molecule and the THEIC bridge. We fixed the position of the Si ions, and their accompanying OH groups, to simulate the attachment of the bridge to the inorganic SiO₂ portion of the PMO. The fixed ions are marked with anchors in Figure S9. We then calculated the adsorption energy of the CO_2 molecule onto different adsorption points on the THEIC structure. The adsorption energy (*E*^{ad}) was calculated as:

$$E^{\text{ad}} = E(\text{THEIC}+\text{CO}_2) - E(\text{THEIC}) - E(\text{CO}_2).$$

Here, $E(\text{THEIC+CO}_2)$ is the total density functional energy of the THEIC bridge with CO₂ molecule attached, E(THEIC) is the total density functional energy of the THEIC bridge studied in the previous section, and $E(\text{CO}_2)$ is the total energy of the carbon dioxide molecule. Adsorption is stable only if E^{ad} is negative. In total, five such adsorption points were considered, four of which were not stable. The unstable points are marked with starts in Figure S9. The only stable adsorption point was the configuration in which the C atom in the CO₂ molecule bonded to the doubly bonded O atom of the THEIC arm. The adsorption energy, in this case, was -0.467 eV. This adsorption energy was mainly driven by the van der Waals interaction. We quantified the role of the van der Waals interaction by repeating the simulation without the inclusion of the van der Waals term—GGA only— E^{ad} changed to -0.103 eV, substantially less stable. Finally, to examine the stability structure at ambient,⁹ we ran a room temperature *ab initio* molecular dynamics simulations based on a micro-canonical ensemble with steps of 0.1 fs for 10 ps. This adsorption point was stable as the CO₂ molecule remained tightly bonded to the THEIC bridge.

We, therefore, demonstrated the significant role of the van der Waals interaction in binding the CO_2 molecule to the THEIC bridge. Similarly, the van der Waals interaction has also been

identified as a considerable contributing factor to the adsorption of CO_2 to the organic part of many organic/inorganic systems and metal-organic frameworks. Here are some examples to mention a few: the adsorption of CO_2 onto Mg-MOF74 and Ca-BTT,¹⁰ onto M/DOBDC (M = Mg, Ni, Co) and Cu-HKUST-1,¹¹ onto Siliceous MFI and DDR,¹² and C₃N.¹³



Figure S9. The schematic of the THEIC bridge anchored to $Si(OH)_3$ terminals interacting with the CO_2 molecule. The numbers in the figure represents the following atoms: 1 = N, 2 = O, 3 = O, 4 = ring.

6. Experimental section

Synthesis of 1,3,5-tris(2-(3-(triethoxysilyl)propoxy)ethyl)-1,3,5-triazinane-2,4,6trione (THEIC bridge): For the synthesis of this organosiloxane bridge, THEIC (3 mmol, 0.783 g) was added to (3-isocyanatopropyl)triethoxysilane (1 mmol, 0.5 mL) in a glass vial, degassed with argon and stirred at 160 °C for 3 h. Then, the temperature was reduced to 120 °C and stirred for 6 h. Finally, a colorless viscous liquid was collected as a product (it was named THEIC bridge) and used for the next step.

General procedure for the synthesis of PMO-THEIC: The synthesized THEIC bridge was employed in the synthesis of a new PMO. A Pluronic triblock copolymer P123, purchased from Sigma-Aldrich (2 g, MW = 5800 g.mol⁻¹), was dissolved in HCl aqueous solution (0.5×10^{-1} M, 75 mL) and stirred for 3 h. Then, the as-synthesized THEIC organosiloxane bridge from the last step was mixed with TEOS with the molar ratio of 1:15, respectively, added to the P123/HCl aqueous solution and stirred for 24 h at 25 °C while the final pH was set at 5. After 24 h, the reaction mixture was transferred to the autoclave for aging for 24 h at 100 °C. After aging, the structure-directing agent (SDA), P123, was extracted from the final product using Soxhlet with MeOH for 4 days. The final product was obtained after drying at 60 °C for 4 h in an oven.

7. References

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