Electronic Supplementary Information (ESI)

for

Efficient cycloaddition of epoxides and carbon dioxide over novel

organic-inorganic hybrid zeolite catalysts

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Experimental

Synthesis of Structure-Directing Agents (SDAs)

The SDAs were synthesized in two steps according to previous report [1]. Firstly, 0.01 mol of *N*,*N*-dimethyloctadecylamine and 0.1 mol of 1,6-dibromohexane were dissolved into 300 mL mixture of acetonitrile and toluene (1:1 volume ratio). The mixture was then heated and stirred at 343 K for 16 hours. After evaporating the solvents, the first-step product $[C_{18}H_{37}Me_2N^+(CH_2)_6]Br^-$, designated as C_{18-6-0} , was gained. Secondly, 0.01 mol of C_{18-6-0} was mixed with 0.02 mol of tripropylamine in chloroform, stirred under refluxing conditions for 16 hours. The final product of $[C_{18}H_{37}Me_2N^+(CH_2)_6N^+Pr_3]Br^{2-}$ (designated as C_{18-6-3}) was acquired via filtration and vacuum drying. To compare the stability of different SDAs in the final product, Gemini surfactant $[C_{22}H_{45}Me_2N^+(CH_2)_6N^+Me_2C_6H_{13}]Br_2^{-}$ (C_{22-6-6}) with two methyl group as the head group, instead of two propyl group in C_{18-6-3} , was synthesized following literature.²

Synthesis of Lamellar MFI-Type Zeolite

MFI-type lamellar zeolites were synthesized with a gel composition of 100 TEOS : 10 SDA : 24 NaOH: 3970 H₂O. Firstly, SDA of C_{18-6-3} and NaOH was dissolved in water and stirred till a clear solution was gained. Then, TEOS was added dropwise into this solution and stirred at room temperature for 30 minutes. The resultant gel was heated at 333 K for 1 hour, getting rid of ethanol formed from the hydrolysis of TEOS. The resultant homogeneous gel was transferred into a Teflon-lined stainless steel autoclave, in which the crystallization was continued at 423K for 5 days. The solid product was filtered, washed with deionized water and dried at 353 K in air overnight. The as-synthesized organic-inorganic material was designated as LMFI - AS.

For control experiments, C_{22-6-6} was employed as SDA to synthesize lamellar MFI (denoted as LMFI- C_{22} -AS) in a similar procedure as abovementioned LMFI -AS.

Acid treatment of LMFI-AS

In order to prepare anion-exchanged materials, the as-synthesized organicinorganic zeolite was treated with hydrogen halogen acids including hydrogen chloride acid, hydrogen bromide acid and hydrogen iodide acid. Typically, 1g of zeolite was extracted in 30mL of 1.0 M HX/EtOH solution (X stands for Cl, Br or I) at 333 K for 3 hours. The extraction was repeated at the same conditions to confirm whether the physically adsorbed SDAs species were completely removed from the solid. The acid washed and dried samples were designated as LMFI-X (X = Cl, Br or I). For comparison of pore volume and surface area, a portion of LMFI-X samples were also calcined at 823 K in air for 6 hours to burn off the organic SDAs, giving rise to LMFI-X-cal samples.

Synthesis of Silicalite-1

To compare with the catalytic performance of lamellar MFI zeolite, a conventional silicalite-1 with three-dimensional MFI structure was hydrothermally synthesized

using tetrapropylammonium hydroxide (TPAOH) as structure-directing agent. 30 g TEOS was added into the mixture of 22.5 g water and 7.5 g TPAOH (20wt.%). The mixture was magnetically stirred for 30 minutes till the TEOS was hydrolyzed. After removing ethanol formed, the gel was then crystalised in a Teflon-lined stainless steel autoclave at 423 K for 48 hours. The product was filtered, washed with distilled water and dried at 353 K overnight. The as-synthesized silicalite-1 was similarly washed with 1M HI/EtOH solution as mentioned above, leading to a final product designated as S-1-I.

Characterization Methods

The powder X-ray diffraction patterns were recorded on a Rigaku Ultima IV X-ray diffractometer using Cu-K α radiation (λ =1.5405 Å) at 35 kV and 30 mA. The nitrogen adsorption isotherms were recorded at 77 K on a BELSORP-MAX instrument after activating the samples at 393 K overnight. The SEM images were taken on a Hitachi S-4800 Scanning electron microscope. The TEM images were collected on a TECNAI G2F30 Transmission Electron microscope. The quantity of organic species was measured by elementary analysis on ElementarVario EL III analyzer. Ion-chromatography was conducted on Dionex ICS-2500 for halogen quantification. The thermogravimetric and differential thermal analyses (TG-DTA) were performed on a NETZSCH STA 449 F3 Jupiter Thermal analyzer.

Catalytic Reactions

The cycloaddition of carbon dioxide into epoxides was conducted in a high pressure autoclave reactor. For a typical run, 10 mmol of substrate and 100 mg of Catalysts were charged into a 50 mL Teflon-lined autoclave equipped with a magnetic stirrer. Cyclohexanone (0.15 g) was added as an internal standard. The autoclave was first purged with carbon dioxide for three times to get rid of the air inside. Then, 2.0 MPa of carbon dioxide was dosed into the reactor for 10 minutes, allowing CO₂ gas to

dissolve into the reaction mixture. The autoclave was heated and stirred in oil bath at 413 K for 4 hours. After the reaction was completed, the autoclave was cooled down in an ice bath for 15 minutes. After the gas inside was released gently, the reaction mixture was separated from the solid catalyst by centrifugation. The resultant mixture was analyzed by gas chromatography (SHIMADZU GC2014) equipped with a RTX@Wax capillary column (30 m 0.25mmID 0.25 μ m) and a flame ionization detector. GC-MS (Agilent 6890A/5973N) was employed to identify the products.

Turnover number (TON) was calculated by referring the amount of converted epoxide to that of halogen contained in the catalysts.

References

- K. Na, M. Choi, W. Park, Y. Sakamoto, O. Terasaki, R. Ryoo, J. Am. Chem. Soc., 2010, 132, 4169.
- M. Choi, K. Na, J. Kim, Y. Sakamoto, O. Terasaki, R. Ryoo, *Nature*, 2009, 461, 246.



Fig. S1 Powder X-ray diffraction patterns of silicalite-1 with three-dimensional MFI structure (a), as-synthesized lamellar MFI zeolite, LMFI-AS (b) and hydrogen iodide acid-treated lamellar MFI zeolite, LMFI-I (c).



Fig. S2 TG and DTG curves of LMFI-AS and LMFI-I.



Fig. S3 TG and DTG curves of lamellar MFI zeolites as-synthesized with C_{18-6-3} (upper) and C_{22-6-6} (down) and after treated with 1 M HCI/EtOH solution at different conditions. The peak between 573K- 693K on DTG graph is belongs to SDA stuck inside zeolite framework.

The stabilities of C_{18-6-3} and C_{22-6-6} SDAs occluded within zeolite crystals were investigated by multi-step acid treatment. LMFI-AS and LMFI-C₂₂-AS materials were

first washed with 1 M HCl/EtOH at 333 K for 3 hours repeatedly, leading to LMFI -AT and LMFI-C₂₂-AT. The quantity of SDA inside framework was determined by the mass loss at 573 – 693 K in TGA. The treatments removed 7.2wt.% organic species for LMFI-AS and 3.1wt.% organic species for LMFI-C₂₂-AS. A further acid treatment, conducted with the same concentration of HCl/EtOH but at a higher temperature of 423 K, the product of which is denoted as C₁₈-AT150 and C₂₂-AT150 respectively. The treatment almost made the organic species intact for LMFI-AT, whereas further decreased the organic species by 1.6wt.% for LMFI-C₂₂-AT. The results verified that the acid treatment could remove readily the organic species physically adsorbed or loosely occluded within lamellar zeolites. However, the remaining C₁₈₋₆₋₃ species containing bulky propyl groups were firmly stuck in the intersection of 10-memered ring channels and they were more stable than the C₂₂₋₆₋₆ species against acid washing. Thus, the use of C₁₈₋₆₋₃ as SDA would have the advantage of preparing stable organicinorganic hybrid catalysts.

 C_{22-6-6} SDA



Molecular formula of (a) C_{22-6-6} and (b) C_{18-6-3} SDAs

Cat.	Chemical composition (%)			SDA content ^c S_{BET}^{d}		\mathbf{V}_{total}^{d}
	Ca	Na	X (X=Cl, Br, I) ^b	(%)	$(m^2 g^{-1})$	(cm ³ g ⁻¹)
S-1-I	9.1	0.69	0	10.4	1.9	0.01
LMFI-AS	20.0	0.87	-	28.1	80	0.19
LMFI-I	12.8	0.39	1.94	18.6	239	0.35
LMFI-Cl	13.9	0.64	1.92	18.0	118	0.20
LMFI-Br	12.8	0.74	0.49	16.1	214	0.30

Table S1 Physicochemical properties of LMFI and S-1 samples

^a Determined by elemental analysis.

^b Quantified by ion chromatography.

^c Measured by thermal thermogravimetric analysis.

 d Measured by N₂ adsorption at 77 K.



Fig. S4 Influence of reaction conditions on the cycloaddition of CO_2 to ECH over LMFI-I.

(A) Effect of reaction temperature; (B) Effect of CO₂ pressure; (C) Effect of reaction time; (D) Effect of catalyst amount.

Optimal reaction conditions: temperature, 413 K; CO₂ pressure, 2.0MPa; reaction time, 4 h; catalyst amount, 100 mg; substrate, epichlorohydrin, 10 mmol. Each graph was obtained under optimized reaction parameters while keeping the others unchanged.



Fig. S5 The reusability of LMFI-I in the cycloaddition of CO_2 to ECH.

Reaction conditions: cat, 50 mg; ECH, 10 mmol; CO₂ pressure, 2.0 MPa; temp., 423 K; time, 4 h; no solvent.



Fig. S6 TEM image of LMFI-I after catalytic use in the cycloaddition of ECH and CO_2 for 4 times.



Scheme S1 The reaction route for ring opening of epoxides and cycloaddition of CO₂ over organic ammonium-iodide synergistic catalyst.