#### Accepted Manuscript

Title: Metal-free amino-incorporated organosilica nanotubes for cooperative catalysis in the cycloaddition of  $CO_2$  to epoxides

Authors: Shengbo Zhang, Xiao Liu, Mei Li, Yan Wei, Gefei Zhang, Jinyu Han, Xinli Zhu, Qingfeng Ge, Hua Wang



PII:	S0920-5861(18)30112-3
DOI:	https://doi.org/10.1016/j.cattod.2018.07.004
Reference:	CATTOD 11549
To appear in:	Catalysis Today
Received date:	23-2-2018
Revised date:	10-5-2018
Accepted date:	3-7-2018

Please cite this article as: Zhang S, Liu X, Li M, Wei Y, Zhang G, Han J, Zhu X, Ge Q, Wang H, Metal-free amino-incorporated organosilica nanotubes for cooperative catalysis in the cycloaddition of CO<sub>2</sub> to epoxides, *Catalysis Today* (2018), https://doi.org/10.1016/j.cattod.2018.07.004

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

# Metal-free amino-incorporated organosilica nanotubes for cooperative catalysis in the cycloaddition of CO<sub>2</sub> to epoxides

Shengbo Zhang,<sup>a,1</sup> Xiao Liu,<sup>c,1</sup> Mei Li,<sup>a</sup> Yan Wei,<sup>a</sup> Gefei Zhang,<sup>a</sup> Jinyu Han,<sup>a</sup> Xinli Zhu,<sup>a</sup> Qingfeng Ge,<sup>a,b</sup>\* Hua Wang<sup>a</sup>\*

<sup>a</sup>Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering and Technology, Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Tianjin 300072, P. R. China

<sup>b</sup>Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901, United States

<sup>c</sup>Key Laboratory of Pesticide & Chemical Biology of the Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, P. R. China

*E-mail:* <u>tjuwanghua@tju.edu.cn;</u> E-mail: <u>qge@chem.siu.edu</u>

1 These authors contributed equally.

#### **Graphic Abstract**



#### Highlights

- Novel amine-incorporated organosilica nanotubes with large-pore diameter and shortchannel were applied for the cycloaddition of CO<sub>2</sub> to epoxides.
- The remarkably enhanced catalytic performance could be ascribed to the cooperative effect of the silanols and the -NH<sub>2</sub> groups, facilely generated in the channel, as well as the facilitated transport and the hydrophobicity.
- The amine-incorporated organosilica nanotubes catalyst displayed enhanced catalytic activities and recyclability.

**Abstract:** The novel amino-incorporated benzene-bridging organosilica nanotubes (AM-NT) were used to efficiently catalyze the cycloaddition of  $CO_2$  to epoxides, producing cyclic carbonates under mild conditions. The highest activity was achieved on  $AM_{0.4}$ -NT nanotubes with a pore diameter of ~7 nm and a length of ~60 nm in presence of tetrabutylammonium iodide (TBAI). The remarkably enhanced catalytic performance could be ascribed to the cooperative effect of the silanols as acid sites and the amino groups as basic sites, facilely generated in the

channel, as well as the transport of substrates and products facilitated by the nanotubes with large pore diameters and short lengths as well as hydrophobicity. Moreover, the catalyst exhibited effective catalytic activity for a broad range of epoxides with a reasonable reusability.

Keywords: cycloaddition of CO<sub>2</sub> to epoxides; organosilica nanotubes; amine-incorporated; cooperative catalysis.

#### 1. Introduction

The increasing emission of carbon dioxide (CO<sub>2</sub>) has been linked to severe global warming and attracted widespread attention in recent years [1-3]. In the context of carbon capture and sequestration, several efficient routes have been developed for chemical fixation of CO<sub>2</sub> in the production of the value-added chemicals [4-9]. Cycloaddition of CO<sub>2</sub> to epoxides to form cyclic carbonates is one of the most promising pathways because of a 100% atom-economy. Cyclic carbonates are widely used as green polar aprotic solvents, monomers for plastics and pharmaceuticals, and electrolytes for lithium-ion batteries [10-13]. Homogeneous processes of producing cyclic carbonate are limited by the loss of catalysts in recycling and high cost of products separation. In contrast, processes using the heterogeneous catalysts, especially porous materials such as zeolites [14-15], metal-organic frameworks (MOFs) [16-21], porous materials/supported ionic liquids [22-25], and functional polymers [26-31] overcome those limitations of the homogeneous processes.

Despite of enormous progress being made on the design and synthesis of efficient heterogeneous catalysts for cyclic carbonates, the catalytic activity remains lower, especially for epoxides with large molecular size, due mainly to the diffusion limit. For example, the highly porous metal-organic framework incorporating metal sites and nitrogen-rich groups [17-19] and

a periodic mesoporous organosilica with a basic urea-derived framework (PMO-UDF) [32] have been shown to catalyzed addition of CO<sub>2</sub> to epoxides to produce cyclic carbonates. In particular, those materials exhibited an excellent catalytic efficiency toward small molecular size epoxides. Unfortunately, for epoxide with a large molecular size, the activity of those materials decreases sharply, due to slow diffusion in small pores of MOFs (~1 nm in diameter) and PMO-UDF (~2 nm in diameter). Additionally, improvements of thermal and chemical stabilities are needed for those materials as a practical catalyst. Eliminating metal active sites in the catalytic material will likely make the process greener and more eco-friendly [16-31].

Organosilica nanotubes have been prepared from bridged organosilane precursors using a sample micelle-templating approach. These nanotubes have several distinct advantages, including large pore size, uniform surface silanols, being easily functionalized, controllable hydrophobicity/hydrophilicity, high surface areas and structural stability [33-37]. The presence of the silanol hydroxyl groups (-OH) can facilitate the ring opening of epoxide. In this case, the hydroxyl group coordinates with the epoxide ring and polarize the C-O bond to form an activated epoxide, which is able to facilely undergo ring-opening upon nucleophilic attacks by Br or I [38-45]. Several research groups reported that the amino group (-NH<sub>2</sub>) can adsorb and activate  $CO_2$  at ambient pressure [46-50]. Recently, we synthesized a novel solid mesoporous material by one-pot, benzene-bridged organosilica nanotubes containing amino groups in the pore (AM-NT) to support the AuPd nanoparticles for visible-light-driven hydrogen evolution [37]. The -OH and -NH<sub>2</sub> active sites can be facilely generated in the pore by assembling the corresponding precursors during the framework construction. The acid-base pair, silanol and -NH<sub>2</sub> functional group in organosilica materials, are expected to function cooperatively to catalyze the cycloaddition of CO<sub>2</sub> to epoxides. Additionally, AM-NT is hydrophobic due to the presence of

benzene in the organosilica framework. The hydrophobicity is believed to favor the organic transformations in an organic solvent [51-52]. In the presnt stduy, we use AM-NT as metal-free solid catalysts with tetrabutylammonium iodide as a cocatalyst for coupling  $CO_2$  with various epoxides. We found that very short AM<sub>0.4</sub>-NT with ~60 nm in length and ~7 nm in pore diameter exhibited a high initial catalytic avtivity. Furthermore, amino-incorporated benzene-bridging organosilica nanotubes show a reasonable catalytic activity for a broad range of substrates and good reusability.

#### 2. Experimental

#### 2.1 Materials

1,4-bis(triethoxysilyl)benzene (BTEB) and triblock copolymer  $EO_{20}PO_{70}EO_{20}$  (Pluronic P123, Mw = 5800) were purchased from Sigma-Aldrich Company Ltd. (U.S.A.). 3aminopropyltrimethoxysilane (97%), tetraethoxysilane (TEOS) and hexamethyldisilazane (HMDS) were purchased from *J&K*. Other reagents were obtained from Shanghai Chemical Reagent.

#### 2.2 Synthesis of amino-incorporated organosilica nanotubes

Amine-incorporated organosilica nanotubes were synthesized according to the previous report [37]. In a typical synthesis, 0.55 g of P123 and 1.75 g of KCl were dissolved in 150 mL 2 M HCl solution at 38 °C with stirring for 2 h and followed by adding 2.1 mmol of 1,4-bis(triethoxysilyl)benzene (BTEB) with vigorous stirring for an additional 12 h. Then 1.4 mmol of 3-aminopropyltrimethoxysilane (APTMS) was added dropwise, and the mixture was stirred for 24 h (The molar ratio of APTMS to the initial silane mixture was 0.4) before being transferred to a PTFE hydrothermal reactor at 100 °C. After reacting for 24 h, the solid product

was recovered by filtration and followed by drying. Finally, the surfactant was extracted by refluxing the sample in an acid-ethanol solution for 24 h. Deprotonation of the amine groups was achieved by stirring the extracted samples in 0.01 M NaOH aqueous solution. The sample was denoted as AM<sub>0.4</sub>-NT. For comparison, AM-NT samples with 0.1 and 0.2 molar fraction of aminosilane were also synthesized, denoted as AM<sub>0.1</sub>-NT and AM<sub>0.2</sub>-NT, respectively.

#### 2.3 Characterization

The nitrogen adsorption-desorption isotherms were collected on a Micromeritics Trisstar 3000 instrument at 77 K. The specific surface area was estimated according to the Brunauer–Emmett– Teller model. Transmission electron microscopys (TEM) were carried out with a Philips Tecnai G2 F20 system at 200 kV. Solid-state <sup>13</sup>C cross polarization magic-angle spinning (CP MAS) NMR spectra and <sup>29</sup>Si MAS NMR spectra were collected on a 400 MHz instrument.

#### 2.4 AM-NT-Catalyzed cycloaddition of CO<sub>2</sub>

In a typical experiment, a mixture of propylene epoxide (10 mmol), DMF (5 mL), CO<sub>2</sub> (1.0 MPa), AM<sub>0.4</sub>-NT (65 mg for 0.067mmol N) and tetrabutylammonium iodide (TBAI) (0.1 mmol) was added to a stainless steel autoclave equipped with an automatic stirrer and temperature controlling system. The autoclave was flushed three times with CO<sub>2</sub> and pressurized to 1.0 MPa and kept at 70 °C for 10 h for reaction. After the reaction, the catalyst powder was filtered via an organic membrane and the resulting liquid was analyzed by Bruker 456 gas chromatograph equipped with a flame ionization detector (FID).

#### 3. Results and discussion

#### 3.1 Synthesis of amino-incorporated organosilica nanotubes (AM<sub>x</sub>-NT).

The amino-incorporated organosilica nanotubes (AM<sub>x</sub>-NT) with different molar fractions of APTMS were synthesized. According to the detailed characterization in our previous report [37], the AM<sub>x</sub>-NT samples are composed of nanotubes with ~7 nm inner diameter and ~3 nm wall thickness. The lengths of the nanotubes for AM<sub>x</sub>-NT can shortened by increasing the fraction of APTMS. The AM<sub>0.4</sub>-NT has a length of ~60 nm, shorter than >100 nm nanotubes of AM<sub>0.1</sub>-NT and AM<sub>0.2</sub>-NT. The incorporation of the –NH<sub>2</sub> and –OH functional groups in the nanotubes has been confirmed by the results of <sup>29</sup>Si magic angle spinning (MAS) NMR, solid-state <sup>13</sup>C cross polarization magic-angle spinning (CP MAS) NMR and X-ray photoelectron spectroscopy (XPS) analyses. Those characterizations consistently indicate that the silanols and the alkyl-NH<sub>2</sub> groups have been built in the nanotubes successfully.

#### 3.2 AM<sub>x</sub>-NT-catalyzed cycloaddition of CO<sub>2</sub> to epoxides.

Catalytic performances of as-prepared  $AM_x$ -NT catalysts for the cycloaddition of CO<sub>2</sub> to propylene epoxide were evaluated at 70 °C and 1.0 MPa CO<sub>2</sub> for 10 h. The results are shown in Figure 1 and Table 1. The physical properties of the catalysts are listed in Table S1. As shown in Table 1, only trace amount of cyclic carbonate was formed on  $AM_{0.1}$ -NT without TBAI (Entry 1) while only TBAI without catalysts gave a low conversion of 7.2% (Entry 2). Combining  $AM_x$ -NT and TBAI resulted in a significantly increased conversion (Entries 3-5). The best TOF of 80 h<sup>-1</sup> (based on the converted amounts of propylene epoxide by per mmol N) was obtained on  $AM_{0.4}$ -NT. The remarkable enhancement of catalytic activity can be attributed to the effcient ring-openning of propylene epoxide through a mechanism that is similar to that on the silica supported ionic liquid [22-25]. In this case, the acidic surface silanol groups interact with the activate propylene epoxide, which is subsequently attacked by a nucleophile I<sup>-</sup> from TBAI to open the ring. Meanwhile, the amino groups and amine-silanol activate CO<sub>2</sub> and contribute to the

overall enhancement of the catalytic performance. The function of  $-NH_2$  is revealed by the low conversion of 10% when an amino-free NT is used (Figure 5c). Furthermore, both  $AM_{0.1}$ -NT and  $AM_{0.2}$ -NT with longer lengths exhibited lower TOFs of 44 h<sup>-1</sup> and 56 h<sup>-1</sup>, respectivly, than that using  $AM_{0.4}$ -NT as the catalyst. (Entries 3-4). These results demonstrate that short nanotube is necessary for obtaining a high activity. This is expected as a short length enables more efficient transport of reactants and products.



Figure 1. (a) Conversion of cycloaddition of  $CO_2$  to epoxide on  $AM_{0.1}$ -NT,  $AM_{0.2}$ -NT,  $AM_{0.4}$ -NT. (b) Conversion of cycloaddition of  $CO_2$  to epoxide on Gam-NT, NH<sub>2</sub>-MCM-41, NH<sub>2</sub>-SBA-15, NH<sub>2</sub>-SNT and  $AM_{0.4}$ -NT.

For comparison, the catalytic performane of Gam-NT prepared by post-grafting the aminosilane on the organosilica nanotubes was tested. (Scheme S1, Figure 2a, Figures S1-S2). The Gam-NT catalyst only gave a TOF of 19 h<sup>-1</sup> (Entry 6), clearly smaller than those on  $AM_x$ -NT (Entries 3-5). Therefore, one-pot method is advantageous over the post-grafted one. To show the hydrophobic effect on the catalytic performance, the aminosilane was immobilized on the pure silica support using the one-pot method to prepare three catalysts, NH<sub>2</sub>-SBA-15 with 6.4 nm pore (Figure 2b, Figures S3-S5), NH<sub>2</sub>-MCM-41 with 2.9 nm pore (Figure 2c, Figures S6-S7) and

 $NH_2$ -SNT with 7.8 nm pore but without the bridged benzene in the nanotubes framework (Figure 2d, Figures S8-S9), respectively. All three catalysts exhibited lower TOFs of 30 h<sup>-1</sup>, 24 h<sup>-1</sup> and 36 h<sup>-1</sup> (Entries 7-9) than those of the  $AM_x$ -NT series. These results showed that the longer nanotubes with less hydrophobicity limit transport of the reactants and products through the pores. In the case of  $NH_2$ -MCM-41, small pore diameters cause diffusion limitation. Additionally, amine-free organosilica nanotube (Entry 10) gave 22% conversion, much higher than that of TBAI alone. It demonstrated that the silanol groups play an effective role in activating epoxides.



Figure 2. The TEM images of (a) Gam-NT, (b) NH<sub>2</sub>-SBA-15, (c) NH<sub>2</sub>-MCM-41 and (d) NH<sub>2</sub>-SNT.

The above results demonstrate that the dual catalyst system  $AM_{0,4}$ -NT with TBAI showed much higher TOF than other tested catalysts. The enhanced activity can be attributed to effective activation of CO<sub>2</sub> and propylene epoxide through the cooperative catalysis of the acidic silanol, basic amino groups in presence of a nucleophile I<sup>-</sup> anion, and the effective transport of the reactant and product facilitated by the large-pore size, short pore length as well as hydrophobicity of the pores.

<b>Table 1.</b> Cycloaddition of $CO_2$ to epoxides with different cataly
---

$\int_{-\infty}^{\infty} + CO_2 \xrightarrow{Catalyst}_{T, P} \xrightarrow{O}_{T, P}$								
Entry	Catalysts	Pore size	Co-catalyst	Conversion	TOF <sup>b</sup>			
		(nm)		(%)	(h <sup>-1</sup> )			
1	AM <sub>0.1</sub> -NT	7.5		Traces	-			
2	-	-	TBAI	7.2	-			
3	AM <sub>0.1</sub> -NT	7.5	TBAI	95	44			
4	AM <sub>0.2</sub> -NT	7.3	TBAI	99	56			
5	AM <sub>0.4</sub> -NT	6.8	TBAI	99	80			
6	Gam-NT	6.5	TBAI	67	19			
7	NH <sub>2</sub> -SBA-15	6.4	TBAI	85	30			
8	NH <sub>2</sub> -MCM-41	2.9	TBAI	79	24			
9	NH <sub>2</sub> -SNT	7.8	TBAI	90	36			
10	NT	7.9	TBAI	22	-			

<sup>a</sup>Reaction conditions: substrate (10 mmol), solvent (DMF, 5 mL), catalysts (0.067 mmol N), TBAI (0.1 mmol), 1.0 MPa CO<sub>2</sub>, 70 °C, 10 h. <sup>b</sup>TOF was calculated from the data within the first 1 h and according to the following equation: TOF = mmol<sub>converted propylene epoxide</sub> / (mmol<sub>N</sub> × h).

#### 3.3 Effects of reaction conditions.

The effect of different reaction conditions such as  $CO_2$  pressure and reaction temperature on propylene carbonate synthesis were investigated. As shown in Figure 3a, the  $CO_2$  pressure had a significant impact on the conversion of propylene epoxide. The conversion of propylene epoxide was dramatically increased from 60% to 98% with the increase of  $CO_2$  pressure from 0.2 MPa to 1.0 MPa, and remained nearly constant in the range of 1.0-3.0 MPa. However, further increasing  $CO_2$  pressure to 4.0-5.0 MPa resulted in a lower conversion of 82% propylene epoxide. The reason is that the exceedingly high  $CO_2$  pressure may block the interaction between the catalyst and propylene epoxide, and cause a low concentration of propylene epoxide in the vicinity of the catalyst (so-called dilution effect) [32,53-57]. Hence, a mild  $CO_2$  pressure of 1.0 MPa was used in our experiment. The effect of reaction temperature was also investigated. As shown in Figure 3b, the conversion of propylene epoxide increases with the increasing reaction temperature in the range of 25-70 °C and levels off upon further increasing reaction temperature to 120 °C.



**Figure 3.** Influence of reaction conditions of (a) CO<sub>2</sub> pressure and (b) reaction temperature on propylene epoxide conversion.

#### 3.4 $AM_{0.4}$ -NT for cycloaddition of $CO_2$ to other epoxides.

We further extend the application of the metal-free amino-functionalized nanotubes as catalysts for cycloaddition of CO<sub>2</sub> to substituted epoxides (Table 2). As shown in Table 2, high activity and selectivity were achieved for various terminal epoxides with either electronwithdrawing or electron-donating groups (Entries 1-7). Furthermore, the relatively less reactive subustrates, cyclopentene oxide and cyclohexene oxide, were also applied (Entries 8-9). However, the lower activities were observed due to the steric hindrance originated from the two rings in the substrate [43]. Notably, AM<sub>0.4</sub>-NT could effectively catalyze the cycloaddition of CO<sub>2</sub> to epoxides with large molecular sizes (Entries 5-7), achieving a high conversion and selectivity in 12 h. This reaction time is less than that reported on either MOFs or PMO [18, 19, 32] as the catalyst. Obviously, AM<sub>0.4</sub>-NT with a large pore diameter (~7 nm) and short length has the advantage over those materials with small pore diameters (MOFs ~ 1 nm and PMO ~ 2 nm).

·			
		98	99
2		96	99
3 CI	ci , , , , , , , , , , , , , , , , , , ,	99	99
	но	95	99
5		95	99
	CI L	92	99
Br	Br		

**Table 2.** Cycloaddition of CO<sub>2</sub> to various epoxides catalyzed by AM<sub>0.4</sub>-NT.<sup>a</sup> Product

Conversion/%

Substrate

Entry

Selectivity/%



<sup>a</sup>Reaction conditions: substrate (10 mmol), solvent (DMF, 5 mL), AM<sub>0.4</sub>-NT (65 mg), TBAI (0.1 mmol), 1.0 MPa CO<sub>2</sub>, 70 °C, 12 h.

#### 3.5 Reusability of $AM_{0,4}$ -NT in catalytic cycloaddition of $CO_2$ to propylene epoxide.

The reusability experiments were performed at 6 h intervals to confirm the stability of the AM<sub>0.4</sub>-NT under 70 °C and 1 MPa. After the reaction, the AM<sub>0.4</sub>-NT was recovered by filtration and reused for the next run. As shown in Figure 4a, there was no significant decrease in conversion (>92%) and selectivity (99% for propylene carbonate) after the 6<sup>th</sup> cycle. Furthermore, the analysis of the recovered catalyst by TEM, nitrogen adsorption-desorption and <sup>13</sup>C CP MAS NMR (Figure 4b,c,d) indicated the structure and the composition were maintained after six cycles. These results indicate that AM<sub>0.4</sub>-NT has an excellent reusability.



**Figure 4.** (a) The recycling performance of  $AM_{0.4}$ -NT for cycloaddition of CO<sub>2</sub> to epoxide; (b) The TEM image, (c) Nitrogen adsorption-desorption isotherms and (d) <sup>13</sup>C CP MAS NMR spectrum of  $AM_{0.4}$ -NT after the 6<sup>th</sup> reaction.

#### 3.6 Reaction mechanism

Based on the present results and previous reports [27, 43, 53-57], a possible mechanism can be proposed for the cycloaddition of CO<sub>2</sub> to epoxides to form cyclic carbonates on the AM<sub>x</sub>-NT catalysts (Scheme 1). Initially, the acidic silanols uniformly built in the pores, which act as the proton donors to form hydrogen bonds with the oxygen atoms of the epoxides and help to polarize the C-O bond. Subsequently, the nucleophilic I<sup>-</sup> anion attacks the less hindered  $\beta$ -carbon atom of epoxide to open the epoxy ring. Silanol-NH<sub>2</sub> interaction help to adsorb and activate CO<sub>2</sub> as well as facilitate coupling of the activated CO<sub>2</sub> with the ring-opened intermediate to form the carbonate intermediate. Finally, the intramolecular ring-closure occurs to generate the cyclic carbonate, liberating the AM<sub>0.4</sub>-NT and TBAI catalysts. The cooperative effect of silanol groups,

-NH<sub>2</sub> groups and co-catalyst TBAI enables the reaction to proceed effectively under mild conditions.



Scheme 1. Proposed reaction mechanism for the AM<sub>0.4</sub>-NT-catalyzed cycloaddition of CO<sub>2</sub> to epoxides.

Herenin, as shown schematically in Figure 5a,  $AM_{0.4}$ -NT-Me, i.e. the silanols of  $AM_{0.4}$ -NT were capped by the trimethylsilyl [-Si(CH<sub>3</sub>)<sub>3</sub>] groups, was utilized to illustrate the cooperative effetct between the -NH<sub>2</sub> groups and the silanols. Figure 5b shows the <sup>29</sup>Si MAS NMR spectrum of the AM<sub>0.4</sub>-NT and AM<sub>0.4</sub>-NT-Me. For AM<sub>0.4</sub>-NT-Me, a new peak at 15 ppm appears due to the trimethylsilane group [-Si(CH<sub>3</sub>)<sub>3</sub>], and the peaks of silicon species <sup>1</sup>T [SiC(OH)<sub>2</sub>(OSi)] and <sup>2</sup>T [SiC(OH)(OSi)<sub>2</sub>] were significantly weakened and even disappeared, while the peak of <sup>3</sup>T [SiC(OSi)<sub>3</sub>] was enhanced. These results support a successful capping of silanol groups. According to the results of the controlled experiments conducted under 1.0 MPa CO<sub>2</sub> and 70 °C for 5 hours (Figure 5c), the pure organosilica nanotubes without amino functional groups (NT) exhibited a lower catalytic activity (10% conversion after 5 h), indicating the critical role of the -

 $NH_2$  groups for cycloaddition reaction. Furthermore, the  $AM_{0.4}$ -NT-Me exhibited a lower catalytic activity (only 36% conversion after 5 h) than  $AM_{0.4}$ -NT in the absence of the -OH groups. These results confirm that the - $NH_2$  groups (basic sites) function synergetically with silanols (acidic sites) to achieve a high activity for the activation of the epoxide as well as  $CO_2$  under mild conditions.



**Figure 5.** (a) The end-capped route of  $AM_{0.4}$ -NT, (b) <sup>29</sup>Si MAS NMR spectrum of the  $AM_{0.4}$ -NT and  $AM_{0.4}$ -NT-Me and (c) catalytic activity of NT,  $AM_{0.4}$ -NT and  $AM_{0.4}$ -NT-Me. Reaction conditions: substrate (10 mmol), solvent (DMF, 5 mL), TBAI (0.1 mmol), 1.0 MPa CO<sub>2</sub>, 70 °C, 5 h.

#### 4. Conclusions

Novel amino-incorporated organosilica nanotubes with large pore diameter and short pore length were successfully applied for catalytic CO<sub>2</sub> conversion in the production of the cyclic carbonates. AM<sub>0.4</sub>-NT in combination with TBAI displayed a remarkable catalytic activity and reusability as compared with other amino-functionalized heterogeneous catalysts. The present study demonstrated that a cooperative mechanism between the acidic hydroxyls of silanols and basic -

 $NH_2$  groups from the alkyl - $NH_2$  groups is in action for an enhanced catalytic activity. Furthermore, the nanotubes with short lengths and large diameters efficiently reduce the diffusion limitation and improve the reactivity. We also demonstrated that the  $AM_{04}$ -NT catalyst is effective for  $CO_2$  reaction with a broad range of epoxides. Although the functionalized organosilica nanotubes were only tested for the cycloaddition reaction, their application as solid catalysts in metal-free catalysis involving organic reagents is of great potentials.

#### Acknowledgments

We thank instrumental analysis center of Tianjin University for assistance with TEM and NMR analysis. This work was supported by the National Key Research and Development Program of China (2016YFB0600900) and the National Natural Sciences Foundation of China (Grant No.21576204, 21373148, 21206117 and U1662109).

#### References

- S. J. Datta, C. Khumnoon, Z. H. Lee, W. K. Moon, S. Docao, T. H. Nguyen, I. C. Hwang, D. Moon, P. Oleynikov, O. Terasaki, K. B. Yoon, Science 350 (2015) 302–306.
- [2] R. S. Haszeldine, Science 325 (2009) 1647–1652.
- [3] E. S. Sanz-Pérez, C. R. Murdock, S. A. Didas, C. W. Jones, Chem. Rev. 116 (2016) 11840–11876.
- [4] X. B. Lu, D. J. Darensbourg, Chem. Soc. Rev. 41 (2012) 1462-1484.
- [5] X. C. Kang, Q. G. Zhu, X. F. Sun, J. Y. Hu, J. L. Zhang, Z. M. Liu, B. X. Han, Chem. Sci., 7 (2016) 266–273.
- [6] A. Goeppert, M. Czaun, G. K. S. Prakash, G. A. Olah, Energy Environ. Sci., 5 (2012) 7833–7853.
- [7] B. Yu, J.-N. Xie, C.-L. Zhong, W. Li, L.-N. He, ACS Catal, 5 (2015) 3940-3944.

- [8] X. H. Liu, J. G. Ma, Z. Niu, G. M. Yang, P. Cheng, Angew. Chem. Int. Ed. 54 (2015) 988-991.
- [9] Q.-W. Song, Z.-H. Zhou, L.-N. He, Green Chem., 19 (2017) 3707-3728.
- [10] D. J. Darensbourg, Chem. Rev., 107 (2007) 2388–2410.
- [11] A. Decortes, A. Castilla, A. Kleij, Angew. Chem. Int. Ed. 2010, 49, 9822-9837.
- [12] J. Wang, Y. Zhang, Green Chem., 18 (2016) 5248-5253.
- [13] M. North, R. Pasquale, C. Young, Green Chem., 12 (2010) 1514–1539.
- [14] J. Dong, P. Cui, P. F. Shi, P. Cheng, B. Zhao, J. Am. Chem. Soc. 137 (2015) 15988-15991.
- [15] T. H. Bae, M. R. Hudson, J. A. Mason, W. L. Queen, J. J. Dutton, K. Sumida, K. J. Micklash, S. S. Kaye, C. M. Brown, J. R. Long, Energy Environ. Sci. 6 (2013) 128–138.
- [16] T. He, B. Ni, X. Xu, H. Li, H. Lin, W. Yuan, J. Luo, W. Hu, X. Wang, ACS Appl. Mater. Interfaces, 9 (2017) 17969-17976.
- [17] R. Zou, P. Z. Li, Y. F. Zeng, J. Liu, R. Zhao, H. Duan, Z. Luo, J. G. Wang, R. Zou,
  Y. Zhao, Small, 12 (2016) 2334-2343.
- [18] P. Z. Li, X. J. Wang, J. Liu, J. S. Lim, R. Zou, Y. Zhao, J. Am. Chem. Soc. 138 (2016) 2142-2145.
- [19] Y.-H. Han, Z.-Y. Zhou, C.-B. Tian, S.-W. Du, Green Chem., 18 (2016) 4086-4091.
- [20] W. Y. Gao, Y. Chen, Y. Niu, K. Williams, L. Cash, P. J. Perez, L. Wojtas, J. Cai,
  Y. S. Chen, S. Q. Ma, Angew. Chem. Int. Ed. 53 (2014) 2615-2619.
- [21] Z. R. Jiang, H. W. Wang, Y. L. Hu, J. L. Lu, H. L. Jiang, ChemSusChem 8 (2015) 878–885.
- [22] L. G. Ding, B. J. Yao, W. L. Jiang, J. T. Li, Q. J. Fu, Y. A. Li, Z. H. Liu, J. P. Ma,
  Y. B. Dong, Inorg. Chem, 56 (2017) 2337-2344.
- [23] W. Wang, C. Li, L. Yan, Y. Wang, M. Jiang, Y. Ding, ACS Catal, 6 (2016) 6091-6100.
- [24] J. Tharun, K.-M. Bhin, R. Roshan, D. W. Kim, A. C. Kathalikkattil, R. Babu, H. Y. Ahn, Y. S. Won, D.-W. Park, Green Chem., 18 (2016) 2479-2487.
- [25] S. M. Sadeghzadeh, Green Chem., 17 (2015) 3059-3066.

- [26] Y. Du, H. Yang, S. Wan, Y. Jin, W. Zhang, J. Mater. Chem. A, 5 (2017) 9163-9168.
- [27] Q. Sun, B. Aguila, J. Perman, N. Nguyen, S. Ma, J. Am. Chem. Soc, 138 (2016) 15790-15796.
- [28] G. Ji, Z. Yang, H. Zhang, Y. Zhao, B. Yu, Z. Ma, Z. Liu, Angew. Chem. Int. Ed., 55 (2016) 9685-9689.
- [29] Z. Dai, Q. Sun, X. Liu, C. Bian, Q. Wu, S. Pan, L. Wang, X. Meng, F. Deng, F.-S. Xiao, J. Catal, 338 (2016) 202-209.
- [30] J. Wang, J. G. Wei Yang, G. Yi, Y. Zhang, Chem. Commun, 51 (2015) 15708-15711.
- [31] Y. Xie, T. T. Wang, X. H. Liu, K. Zou, W. Q. Deng, Nat. Commun, 4 (2013) 1960-1966.
- [32] M. Liu, X. Lu, L. Shi, F. Wang, J. Sun, ChemSusChem, 10 (2017) 1110-1119.
- [33] X. Liu, X. B. Li, Z. Guan, J. Liu, J. Zhao, Y. Yang, Q. H. Yang, Chem. Commun., 47 (2011) 8073-8075.
- [34] S. Zhang, H. Wang, M. Li, J. Han, X. Liu, J. Gong, Chem. Sci., 8 (2017) 4489-4496.
- [35] S. Zhang, H. Wang, M. Li, J. Han, S. Inagaki, X. Liu, Dalton Trans., 46 (2017) 9369-9374.
- [36] X. Liu, Y. Goto, Y. Maegawa, T. Ohsuna, S. Inagaki, APL Mater., 2 (2014) 113308-113314.
- [37] S. Zhang, H. Wang, L. Tang, M. Li, J. Tian, Y. Cui, J. Han, X. Zhu, X. Liu, Appl. Catal. B Environ. 220 (2018) 303-313.
- [38] J. Wang and Y. Zhang, ACS Catal, 6 (2016) 4871-4876.
- [39] W. Wang, C. Li, L. Yan, Y. Wang, M. Jiang and Y. Ding, ACS Catal, 6 (2016) 6091-6100.
- [40] W.-H. Zhang, P.-P. He, S. Wu, J. Xu, Y. Li, G. Zhang, X.-Y. Wei, Appl. Catal. A Gen, 509 (2016) 111-117.
- [41] X.-D. Lang, Y.-C. Yu, L.-N. He, J.Mol. Catal. A Chem, 420 (2016) 208-215.
- [42] J. Sun, J. Wang, W. Cheng, J. Zhang, X. Li, S. Zhang and Y. She, Green Chem, 14 (2012) 654-660.

- [43] V. B. Saptal, T. Sasaki, K. Harada, D. Nishio-Hamane, B. M. Bhanage, ChemSusChem, 9 (2016) 644-650.
- [44] T. Takahashi, T. Watahiki, S. Kitazume, H. Yasuda and T. Sakakura, Chem. Commun, 0 (2006) 1664-1666.
- [45] A. M. Hardman-Baldwin and A. E. Mattson, ChemSusChem, 7 (2014) 3275-3278.
- [46] R. Srivastava, D. Srinivas, P. Ratnasamy, Micropor. Mesopor. Mater. 90 (2006) 314–326.
- [47] S-M. Hong, S. H. Kim, K. B. Lee, Energy Fuels, 27 (2013) 3358-3363.
- [48] T. C. dos Santos, S. Bourrelly, P. L. Llewellyn, J. W. Carneiro, C. M. Ronconi, Phys. Chem. Chem. Phys, 17 (2015) 11095-11102.
- [49] T. H. Nguyen, S. Kim, M. Yoon, T. H. Bae, ChemSusChem, 9 (2016) 455-461.
- [50] G. S. Foo, J. J. Lee, C-H. Chen, S. E. Hayes, C. Sievers, C. W. Jones, ChemSusChem, 10 (2017) 266-276.
- [51] D. Kim, D. W. Kim, O. Buyukcakir, M.-K. Kim, K. Polychronopoulou, A. Coskun, Adv. Funct. Mater, 27 (2017) 1700706-1700713.
- [52] J. Sun, H. Wang, X. Gao, X. Zhu, Q. Ge, X. Liu, J. Han, Micropor. Mesopor. Mater., 247 (2017) 1-8.
- [53] Z.-Z. Yang, L.-N. He, C.-X. Miao, S. Chanfreau, Adv. Synth. Catal, 352 (2010) 2233-2240.
- [54] J.-Q. Wang, D.-L. Kong, J.-Y. Chen, F. Cai, L.-N. He, J. Mol. Catal. A, 249 (2006) 143-148.
- [55] M. Liu, J. Lan, L. Liang, J. Sun and M. Arai, J. Catal, 347 (2017) 138-147.
- [56] H. Li, C. Li, J. Chen, L. Liu, Q. Yang, Chem. Asian J, 12 (2017) 1095-1103.
- [57] S. Jayakumar, H. Li, Y. Zhao, J. Chen, Q. Yang, Chem. Asian J, 12 (2017) 577-585.