

# Zirconium triflate grafted on SBA-15 as a highly efficient solid acid catalyst for ring opening of epoxides by amines and alcohols



Kamlesh N. Tayade <sup>a</sup>, Lianyue Wang <sup>a</sup>, Sensen Shang <sup>a</sup>, Wen Dai <sup>a</sup>, Manish Mishra <sup>b</sup>, Shuang Gao <sup>a,\*</sup>

<sup>a</sup> Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China
 <sup>b</sup> Department of Chemical Engineering And Shah-Schulman Center for Surface Science and Nanotechnology, Faculty of Technology, Dharmsinh Desai University, Nadiad 387001, Gujarat, India

#### ARTICLE INFO

Article

*Article history:* Received 21 November 2016 Accepted 6 January 2017 Published 5 April 2017

Keywords: Epoxide ring opening Acid catalysis Metal triflate Grafted catalyst Mesoporous silica

# 1. Introduction

Ring opening of epoxides is an important transformation in organic synthesis because it provides access to valuable pharmaceuticals and intermediate chemicals [1–5]. Bifunctional molecules of great significance can be synthesized by nucleophilic attack of amines, azides, alcohols, and thiols on epoxide rings. For example,  $\beta$ -alkoxy alcohols are used as intermediates for the synthesis of pharmaceutical compounds, such as antitumor and immunosuppressant drugs [6].  $\beta$ -Amino alcohols are used for synthesizing  $\beta$ -blockers, insecticidal agents, unnatural amino acids, chiral auxiliaries and oxazolines [2–5].

Several studies have reported the synthesis of  $\beta$ -amino alcohols and  $\beta$ -alkoxy alcohols by aminolysis and alcoholysis of epoxides, respectively, using homogeneous and heterogeneous acid catalysts. However, homogeneous catalytic processes are

# ABSTRACT

Metal (Al, Ti, Zr) triflate grafted mesoporous SBA-15 (AlTf/S, TiTf/S, ZrTf/S) samples were synthesized as inexpensive solid acid materials by a simple one-pot-two-step synthesis methodology. These materials were characterized by X-ray diffraction, N<sub>2</sub>-sorption, thermogravimetric analysis, Fourier transform infrared spectroscopy (FT-IR), *in-situ* pyridine FT-IR spectroscopy, and elemental analysis. ZrTf/S was found to be a highly efficient and reusable solid acid catalyst for ring opening of epoxides with amines and alcohols and produced  $\beta$ -amino alcohols and  $\beta$ -alkoxy alcohols respectively under ambient reaction conditions. The ZrTf/S catalyst showed the highest activity, which was attributed to its high acidity compared with that of the Ti and Al containing samples.

© 2017, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier B.V. All rights reserved.

unattractive considering their disadvantages, such as the use of halogenated and/or toxic solvents and the difficultly of separation and poor reusability of the catalyst. Solid acid catalysts, such as sulfonic acid functionalized SBA-15 and Ti-MCM-41 [7], Na-Y zeolite [8], Cu-MOF (Cu(bpy)(H<sub>2</sub>O)<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>(bpy)) [9], mesoporous alumininosilicate [10], Fe(BTC) (where BTC is 1,3,5-benzenetricarboxylate) [11], CuO/SiO<sub>2</sub> [12], Ti-SBA-12 and Ti-SBA-16 [13], sulfonic acid functionalized mesoporous carbon [14], graphite oxide [15], and mesoporous Zr-beta zeolite [16], have been shown to be active and selective for ring opening reactions of epoxides. However, these catalysts also have some limitations, such as the need for longer reaction times [7-15] and non-ambient reaction conditions [11,12,14], and tedious synthesis of the catalyst [7,16]. Therefore, the development of easy to synthesize, more efficient and environmentally benign catalysts is of great importance.

<sup>\*</sup> Corresponding author. Tel/Fax: +86-411-84379728; E-mail: sgao@dicp.ac.cn

This work was supported by the CAS President's International Fellowship Initiative (2016PT028) and the National Natural Science Foundation of China (21273225 and 21403219).

DOI: 10.1016/S1872-2067(17)62794-3| http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 4, April 2017

Metal triflates (especially triflates of lanthanides and transition metals) have received considerable attention as excellent Lewis acid catalysts for several organic reactions over the past two decades [17-22]. Consequently, supported metal triflates have also been synthesized and used for important acid-catalyzed reactions allowing easy separation, good reusability and enhanced activity [23–30]. It is generally preferable for the catalyst to be chemically grafted to rather than physically adsorbed to the support because of the greater stability of chemically grafted systems. In our previous reports, we developed an aluminum triflate grafted on MCM-41 as a cost effective and easily synthesizable catalyst, which showed high acidity and water tolerance in ketalization of glycerol with acetone into solketal at room temperature [31]. In the present work, metal triflates of Al, Zr, and Ti grafted on SBA-15 mesoporous silica (AlTf/S, TiTf/S, and ZrTf/S, respectively) were prepared. We aimed to generalize our one-pot-two-step synthesis methodology and widening the applications of metal triflate grafted catalysts to epoxide ring opening reactions as a more efficient, low cost and environmentally benign catalyst system. SBA-15 mesoporous silica was chosen as the support owing to its high pore size, thick framework walls and good hydrothermal stability and inter-channel connectivity [32].

# 2. Experimental

# 2.1. Materials

Pluronic P123 (PEO-PPO-PEO) polymer was purchased from Sigma. Zirconium propoxide (70%) in propanol was procured form Alfa-Aesar. Tetraethyl orthosilicate (TEOS), HCl (35%), titanium tetraisopropoxide, aluminum isopropoxide, all epoxides, amines and alcohols were purchased from Sinopharm Chemical Reagents Co. Ltd, Energy Chemical and J & K Scientific, China. All the chemicals were used as received without any purification.

#### 2.2. Synthesis of metal triflate grafted SBA-15 samples

Mesoporous silica SBA-15 was prepared by a reported method using pluronic P123 polymer as template under acidic conditions. Typically, 4 g of P123 was dissolved in 30 mL water and 90 mL of HCl solution (2 mol/L). TEOS was added dropwise with stirring to the polymer solution and allowed to stir at room temperature for 15 min. The mixture was then aged at 40 °C for 20 h. The gel produced was transferred to a Teflon-lined stainless steel autoclave and maintained at 80 °C for 2 d for the hydrothermal synthesis. After 2 d, a white solid formed which was filtered, washed with distilled water and then dried at 100 °C overnight. The dry solid powder was then calcined at 550 °C for 4 h under an air flow to remove the template and obtain the final SBA-15 material.

Trifluoromethane sulfonic acid (0.1 g) was dissolved in 25 mL of toluene. This solution was added to a solution containing zirconium propoxide (70% in propanol; 0.2951 g) dissolved in 25 mL of toluene and allowed to react for 2 h at r.t. under stirring. Dried SBA-15 (150 °C for 4 h, 1 g) was then added to this solution and allowed to react for 24 h at r.t. The solid was then filtered and washed with toluene and dichloromethane/acetonitrile (v/v = 1). The solid powder was then dried at 100 °C for 24 h to obtain zirconium triflate grafted on SBA-15 (ZrTf/S) samples. Titanium isopropoxide (0.1895 g) and aluminum isopropoxide (0.1362 g) were used to prepare the titanium and aluminum triflate grafted SBA-15 (TiTf/S and AlTf/S) samples in a similar manner. The metal/Si molar ratio was maintained at 1/25 for all sample preparations. A schematic representation of the ZrTf/S synthesis is shown in Scheme 1. The synthesized catalyst samples were used for aminolysis and alcoholysis of various epoxides by amines and alcohols, respectively (Scheme 2).

# 2.3. Material characterization

Mesoporous SBA-15 and the samples ZrTf/S, TiTf/S and AlTf/S were characterized with the following analytical techniques. Powder X-ray diffraction (XRD) analysis was performed on a PANalytical X'Pert3 powder diffractometer with Cu  $K_{\alpha}$ radiation ( $\lambda$  = 1.5418 Å; 1 Å = 0.1 nm) in the 2 $\theta$  range of 0.5° to  $10^{\circ}$  with a scanning rate of  $0.02^{\circ}$ /s. The N<sub>2</sub> sorption at liquid nitrogen temperature (-196 °C) for determination of pore size and pore volume, and the BET surface area measurements were performed on a Quantachrome Quadrasorb SI. The samples were degassed at 180 °C for 4 h before the measurements. The C, H, S elemental analysis was performed with a VarioEL elemental analyzer. Metal content was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a PerkinElmer OPTIMA 3300DV. A sample (50 mg) was dissolved in 40% HF solution (5-10 drops) followed by addition of a 5 wt% boric acid solution and made up to 100 mL in a volumetric flask. The resulting solutions were then analyzed by



Scheme 1. One-pot-two-step synthesis of ZrTf/S and diagram of the Brönsted (B) and Lewis (L) acid sites in the ZrTf/S sample.



Scheme 2. Ring opening of epoxides by amines and alcohols to synthesis  $\beta$ -amino alcohols and  $\beta$ -alkoxy alcohols.

ICP-AES. Thermogravimetric analysis (TGA) was performed with a NETZSCH STA 449 F3 Jupiter under an air flow of 50 mL/min from 40 to 800 °C. Diffuse reflectance UV-visible spectroscopy was performed with a PerkinElmer LAMBDA 950 UV/Vis/NIR spectrophotometer at r.t.; samples were activated at 100 °C for 1 h prior to the analysis. Fourier transform infrared (FT-IR) spectroscopy was performed with a Thermo Nicolet iS50 FT-IR spectrometer. *In-situ* FT-IR under vacuum with pyridine-adsorbed and pyridine-desorbed samples at different temperatures was performed with a Bruker TENSOR27 instrument. A neat sample disk was evacuated at 10<sup>-2</sup> Pa at 200 °C for 1 h followed by pyridine adsorption for 5 min. FT-IR spectra were then recorded after desorbing pyridine at 100, 150, and 200 °C for 20 min under vacuum. The acidity was calculated from the following equation:

 $C(B) = 1.88 \text{ IA}(B)R^2/W$  $C(L) = 1.42 \text{ IA}(L)R^2/W$ 

where *C* is concentration of B or L sites (mmol/g), IA is the integrated absorbance of B or L band (cm<sup>-1</sup>), *R* is the radius of catalyst disk (cm), and *W* is the mass of the disk (mg).

# *2.4. Catalytic evaluation of metal triflate grafted SBA-15 samples*

Catalytic activity of the synthesized ZrTf/S, TiTf/S and AlTf/S samples was evaluated by aminolysis and alcoholysis of the epoxides. The epoxides were reacted with amines or alcohols at defined reaction conditions in the presence of the activated (100 °C, 2 h) catalyst samples prepared in this study. The reaction mixtures were analyzed by gas chromatography (Agilent 7890) with a GSBP-5 non-polar column and FID detector for measuring epoxide conversion and product selectivity. The products formed in the reactions were characterized by GC-MS (Agilent 9375MSD with 7890A GC) analysis and the data were matched with those reported in the literature. Conversion of epoxide and product selectivity was calculated from the fol-

#### Table 1

Physicochemical properties of SBA-15, ZrTf/S, TiTf/S, and AlTf/S samples.



**Fig. 1.** Powder XRD patterns of SBA-15 and metal triflate grafted on SBA-15 samples.

lowing equations:

# Conversion = (Initial epoxide mass – final epoxide mass)/Initial epoxide mass × 100% Selectivity for **A** = GC Peak area of **A**/GC peak area of all the products × 100%

Similarly, selectivity for product **B** in aminolysis and selectivity for products **C** and **D** in alcoholysis reactions were calculated.

#### 3. Results and discussion

#### 3.1. Characterization of AlTf/S, TiTf/S, and ZrTf/S samples

Various physicochemical characterization results are shown in Table 1. Metal (Al, Zr, Ti) content as measured by ICP-AES showed a metal:Si ratio of 1:24.6, 1:26.5, and 1:24.9 for the AlTf/S, TiTf/S, and ZrTf/S samples, respectively (Table 1). The XRD patterns of the SBA-15, ZrTf/S, TiTf/S, and AlTf/S revealed characteristic reflections of a mesoporous structure showing peaks for (100), (110), and (200) planes at low angles indicating that the mesoporous structure of SBA-15 was intact in all the synthesized samples (Fig. 1). A decrease in the intensity of the X-ray reflection was indicative of grafting of the metal triflates. N<sub>2</sub>-sorption results also revealed a type IV isotherm, and a decrease in surface area, pore size, and volume indicate grafting of the metal triflate moiety to the mesoporous structure of SBA-15 (Table 1, Fig. 2). The SBA-15 sample showed the

Material	S <sub>BET</sub> (m <sup>2</sup> /g)	Pore size (nm)	Pore volume (cm <sup>3</sup> /g)	Si/metal ª 🗕	CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup> (mmol/g)		Amount of C by	Amount of	
					By TGA <sup>b</sup>	By CHS c	CHS (mmol/g)	acidity <sup>d</sup>	
SBA-15	772	7.5	0.95	_	_	—	_	—	
AlTf/S	575	7.6	0.75	24.6	0.58	0.53	_	_	
TiTf/S	552	7.7	0.71	26.5	0.59	0.55	0.60	0.37	
ZrTf/S	514	6.4	0.67	24.9	0.55	0.58	0.61	0.52	

<sup>a</sup> From ICP-AES analysis.

<sup>b</sup>Calculated from mass loss in TGA in temperature range 230–380 °C.

<sup>c</sup>Calculated from C, H, S elemental analysis.

<sup>d</sup> By FT-IR of pyridine adsorbed samples after desorption at 200 °C under vacuum (10<sup>-2</sup> Pa).



Fig. 2.  $N_2$  adsorption-desorption isotherms of SBA-15, ZrTf/S, TiTf/S, and AlTf/S samples.

highest BET surface area of 772 m<sup>2</sup>/g, which decreased to 575, 552, and 514 m<sup>2</sup>/g for the AlTf/S, TiTf/S, and ZrTf/S samples, respectively, after the metal triflate was grated. The TGA analysis results revealed a mass loss of 0.58, 0.59, and 0.55 mmol/g for the AlTf/S, TiTf/S, and ZrTf/S samples respectively in the temperature range of 230 to 380 °C. This mass loss can be attributed to decomposition of the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> moiety present in the samples (Table 1; Fig. 3). The C, H, S elemental analysis showed the presence of 0.53, 0.55, and 0.58 mmol/g of the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> moiety in the AlTf/S, TiTf/S, and ZrTf/S samples, respectively, which is in accordance with the TGA results (Table 1). The amount of C detected in the samples was consistent with the amount of triflate added during synthesis and suggested nearly complete reaction of the alkoxide metal precursor with triflic acid and the silica surface. The FT-IR spectra of these synthesized samples also showed characteristic absorption bands at ~580 and ~645 cm<sup>-1</sup> attributed to the -CF<sub>3</sub> asymmetric deformation and SO3 symmetric deformation vibrations, respectively (Fig. 4) [33-35]. A very weak band observed at ~760 cm<sup>-1</sup> was attributed to C-S stretching vibrations. IR bands at ~1290 and 1030 cm<sup>-1</sup> were attributed to S =0 stretching vibrations, which were observed as a shoulder in all samples (except SBA-15) merged with the characteristic Si-O-Si bands of silica in the same region [7,33-35]. The strong and broad band between 3600 and 3200 cm<sup>-1</sup> was attributed to O-H stretching



Fig. 3. TGA plots of synthesized ZrTf/S, TiTf/S, and AlTf/S samples.



Fig. 4. FT-IR spectra of SBA-15, AlTf/S, TiTf/S, and ZrTf/S samples.

and that at ~1650 cm<sup>-1</sup> was attributed to bending vibrations of water molecules associated with surface silanol groups. These characterization results confirmed the successful grafting of the metal triflates onto the SBA-15 mesoporous surface. Thus, it is likely that our one-pot-two-step metal triflate-grafting approach may be extended to other metal triflates [31].

The FT-IR spectrum measured after in-situ pyridine adsorption under vacuum showed bands at 1546 and 1640 cm<sup>-1</sup>, which were assigned to the pyridinium ions adsorbed at B sites. Bands at 1450 and 1610 cm<sup>-1</sup> were assigned to pyridine adsorbed at L acid sites and a further band at 1490 cm-1 was assigned to pyridine adsorbed to both B and L acid (B+L) sites (Fig. 5) [36-38]. The greatest acidity was observed for ZrTf/S (0.52 mmol/g) (Table 1) while TiTf/S and AlTf/S showed slightly lower acidity (0.37 and 0.34 mmol/g, respectively). The acidity reduced gradually with increasing desorption temperature; however, even after desorption at 200 °C the samples continued to show moderate strength and high acidity. UV-vis diffuse reflectance spectra revealed metal-ligand (O2- and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) charge transfer interactions of the metal in the ZrTf/S, TiTf/S, and AlTf/S samples (Fig. 6) [39–41]. The peak at ~220 nm indicated the presence of tetrahedral coordinated metal centers (CF<sub>3</sub>SO<sub>3</sub>-M-(O-Si)<sub>3</sub>; M = Zr, Ti, Al). The broad absorption band observed in all samples from around 260 to 300 nm could be assigned to octahedral and pentahedral coordinated metal centers generated from interactions with neighboring



**Fig. 5.** FT-IR spectra of pyridine adsorbed ZrTf/S, TiTf/S, and AlTf/S samples indicating L and B acidic sites.



**Fig. 6.** Diffuse reflectance UV-visible spectra of ZrTf/S, TiTf/S, and AlTf/S samples.

hydroxyl groups, as shown in Scheme 1.

3.2. Catalytic evaluation of metal triflate grafted on SBA-15 samples for epoxide ring opening reaction

#### 3.2.1. Reaction condition optimization

For optimization of reaction conditions (Table 2), we initially reacted styrene oxide with aniline in a 25-mL round bottom flask at 25 °C in acetonitrile as a solvent in the presence of 25 mg of the activated (100 °C, 2 h) ZrTf/S sample. These conditions produced 52% conversion of the epoxide and 95% selectivity for the desired  $\beta$ -amino alcohol products (**A**+**B**) at 25 °C. A similar reaction was performed in toluene and under conditions with no solvent. Under these reaction conditions 71% conversion and 94% selectivity was observed in toluene, while the reaction without solvent afforded 91% conversion of the epoxide with 95% selectivity. At 35 °C we achieved an even higher conversion of 94% with 96% selectivity. Thus, the catalytic performance of the ZrTf/S sample was better under solvent free conditions, which can be explained by the fact that dilution of the reaction mixture in the solvent assisted reaction

#### Table 2

Reaction condition optimization for epoxide ring opening of styrene oxide with aniline and with methanol catalyzed by ZrTf/S (25 mg)<sup>a</sup>.

Entry	Temp./Time	Solvent	Epoxide	Selectivity
1	25/20	agatanitrila		(%)
1	25/50	acetoniune	52	95
2	25/30	toluene	71	94
3	25/30	_	91	95
4	35/30	_	94	96
5 (1st recycle)	35/30	—	95	97
6 (2 <sup>nd</sup> recycle)	35/30	—	93	96
7 (3 <sup>rd</sup> recycle)	35/30	—	93	96
8 (4th recycle)	35/30	—	94	95
9	35/10	_	100	98
10 (1st recycle)	35/10	—	98	96
11 (2 <sup>nd</sup> recycle)	) 35/10	—	99	95
12 (3rd recycle)	35/10	—	100	99
13 (4th recycle)	35/10		98	96

<sup>a</sup>Entries 1–8: Styrene oxide (5 mmol), aniline (5 mmol); selectivity for (**A+B**).

Entries 9–13: Styrene oxide (2 mmol), methanol (25 mmol); selectivity for (C+D).



**Fig. 7.** Comparison of catalytic activity of synthesized samples for epoxide ring opening of styrene oxide by aniline. Reaction conditions: styrene oxide (5 mmol), aniline (5 mmol), catalyst (25 mg), 35 °C.

may reduce the product formation rate (Table 2). The solvent had no significant effect on the selectivity of the products. The reusability of the ZrTf/S sample was evaluated for four reaction cycles. In the reusability study for aminolysis, the reaction mixture was filtered after completion of the reaction to separate the used ZrTf/S. The used ZrTf/S sample was washed with petroleum ether and activated at 100 °C for 2 h before the next reaction cycle. In the aminolysis reaction, conversion of styrene oxide and selectivity for the  $\beta$ -amino alcohol were unaffected (94% and 95%, respectively) after four cycles. For a reusability study of alcoholysis, the reaction mixture was filtered after completion of the reaction to separate the used ZrTf/S catalyst. The ZrTf/S sample was directly activated at 100 °C for 2 h before the next reaction cycle. The activity of ZrTf/S was also unaffected after recycling for the alcoholysis reaction up to four reaction cycles (98% conversion of styrene oxide and 96% selectivity for  $\beta$ -alkoxy alcohol (C+D)).

The catalytic activity of the AlTf/S, TiTf/S, and ZrTf/S samples was compared for the ring opening of styrene oxide with aniline (Fig. 7). The ZrTf/S sample clearly showed the highest activity for this reaction giving 94% conversion of the epoxide in 30 min, while the selectivity of all the samples was comparable (>96%). The highest activity of ZrTf/S may be attributed to its stronger Lewis acidity (0.52 mmol/g) than those of the TiTf/S and AlTf/S catalysts (Fig. 5).

#### 3.2.2. Aminolysis of epoxides with amines over ZrTf/S

Various epoxides were then reacted with amines in the presence of the ZrTf/S sample at 35 °C and at an equimolar ratio to explore the substrate scope (Table 3). Styrene oxide reacted with aniline very efficiently to produce  $\beta$ -amino alcohol with 94% conversion of styrene oxide and 91% selectivity for isomer **A** and 96% total selectivity for (**A**+**B**) in 0.5 h. Cyclohexene oxide reacted with aniline to selectively produce the  $\beta$ -amino alcohol with 89% conversion of the epoxide in 1 h. The reactivity of styrene oxide was much higher than that of cyclohexene oxide because the intermediate carbocation formed from styrene oxide is stabilized by resonance with the aromatic ring and is highly susceptible to nucleophilic attack (Scheme 3).

Table 3	
Aminolysis of epoxides with different amines using ZrTf/S (25 mg) at 35 $^\circ \! \mathrm{C}$	•

Enter	Epoxide	Amine	Time	Epoxide conversion	Selectivity for <b>A/B</b>
Entry	(5 mmol)	(5 mmol)	(h)	(wt%)	(wt%)
1	C ⊂ O	H <sub>2</sub> N	0.5	94	91/5
2	O	H <sub>2</sub> N	1	89	100
3	O	H <sub>2</sub> N	3	88	97
4	O	H <sub>2</sub> N CH <sub>3</sub>	3	79	99
5	O	H <sub>2</sub> N OCH <sub>3</sub>	3	78	99
6	O	H <sub>2</sub> N	5 (at 45 °C)	12	83
7	C <sup>o</sup>	H <sub>2</sub> N	5 (at 45 °C)	19	61/7
8	CI	H <sub>2</sub> N	1	100	80/10
9		H <sub>2</sub> N	1	86	79/12
10		H <sub>2</sub> N	1	97	88/6

<sup>a</sup> Entries 2-6: product selectivity includes both stereoisomers (trans- and cis-) and is calculated form GC.



Scheme 3. Plausible reaction pathway of epoxide ring opening reaction over ZrTf/S.

Similarly, the effect of nucleophilicity of the amine was observed in the reaction of cyclohexene oxide with p-Cl, p-CH<sub>3</sub>, and p-OCH<sub>3</sub> aniline, which afforded 88%, 79%, and 78% conversion with 97%, 99%, and 99% selectivity, respectively (Table 3). Cyclohexene oxide also reacted with cyclohexyl amine giving 12% conversion and 83% selectivity after 5 h at 45 °C. The low conversion may be explained by the strong adsorption of the aliphatic amine to acidic sites of ZrTf/S, which caused poisoning of the active sites and lowered product formation. Styrene oxide with cyclohexyl amine also gave reduced product conversion (19%) owing to a similar effect (Table 3). These results demonstrate the excellent activity of the catalyst, even in the presence of highly basic amines. Epichlorhydrin, allylglycidyl ether, and phenyl glycidyl ether also reacted with aniline affording 100%, 86%, and 97% epoxide conversion with 80%, 79%, and 88% selectivity for product isomer A, and 90%, 91%, and 94% total selectivity for (A+B).

#### 3.2.3. Alcoholysis of epoxides with alcohols

The ZrTf/S sample also catalyzed epoxide ring opening with various alcohols efficiently at 35 °C (Table 4). Initially, cyclohexene oxide was reacted with methanol in an equimolar ratio (1:1, 5 mmol), which resulted in 100% conversion of epoxide but only 73% selectivity for the desired product. At higher molar ratios of cyclohexene oxide to methanol (2:25 and 2:50), a very high selectivity for the desired product (96% and 98%) was achieved within 10 min (Table 4). Styrene oxide reacted with methanol to give 100% conversion and 95% selectivity to 2-methoxy-2-phenylethanol (product isomer **C**) at a 2:25 molar ratio in 10 min. Although these conditions gave complete conversion, only 66% selectivity for product isomer **C** was achieved at an equimolar ratio. The by-product formed was

Entry	Epoxide		Alcohol		(min)	Epoxide conversion (wt%)	Selecitivity for C/D (wt%)
1	$\frown$	2 mmol	CH <sub>3</sub> OH	50 mmol	10	100	98
	$\bigcirc$	2 mmol		25 mmol		100	96
		5 mmol		5 mmol		100	73
2	$\sim$	2 mmol	ŶН	25 mmol	15	100	89
		5 mmol		5 mmol		72	30
3	$\sim$	2 mmol	HO	25 mmol	15	100	77
	[℃o	5 mmol	$\bigcup$	5 mmol		99	39
4	()o	2 mmol	OH /	25 mmol	30	99	73
5	Ó	2 mmol	НО	25 mmol	20	100	87
6	$\sim$	2 mmol	CH <sub>3</sub> OH	25 mmol	10	100	95/3
		5 mmol		5 mmol		100	66/2
7		2 mmol	ОН	25 mmol	30	100	62/8
8		2 mmol	HO	25 mmol	15	99	73/8
9		2 mmol	HO	25 mmol	20	97	80/9
10	0	2 mmol		25 mmol	20	100	90/8
		5 mmol	CH30H	5 mmol		47	62/5
11		2 mmol		25 mmol	20	100	95/4
		5 mmol	CH30H	5 mmol		16	93/4
12	CL 2	2 mmol	CH3OH	25 mmol	20	100	90/8

 Table 4

 Alcoholysis of epoxides with different alcohols catalyzed by ZrTf/S (25 mg) at 35 °C<sup>a</sup>.

<sup>a</sup> Entries 1-5: Product selectivity includes both stereoisomers (trans- and cis-) and is calculated form GC.

predominantly the acid catalyzed Meinwald rearrangement product [10] (phenylacetaldehyde), which also highlights the acidic nature of the catalytic sites on the ZrTf/S sample. Secondary, tertiary, and benzylic alcohols also reacted with cyclohexene oxide as well as styrene oxide, to give complete conversion and excellent selectivity at a 2:25 ratio of epoxide to alcohol. Cyclohexene oxide reacted completely with i-propanol and cyclohexanol giving 89% and 77% selectivity in 15 min. Similarly, t-butanol and benzyl alcohol also reacted with cyclohexene oxide with 73% and 87% selectivity in 20 and 30 min, respectively (Table 4). Styrene oxide reacted with t-butanol, benzylalcohol, and cyclohexanol giving 62%, 73%, and 80% selectivity for product isomer C and 70%, 81%, and 89% selectivity for (C+D), respectively, with nearly complete conversion. Such remarkable catalytic activity at low epoxide to alcohol molar ratios and at ambient reaction conditions makes our ZrTf/S catalyst stand out from previously reported Cu-MOF [9], mesoporous aluminosilicate [10], Fe(BTC) [11], CuO/SiO<sub>2</sub> [12], and sulfonic acid functionalized mesoporous carbon [14] based catalysts. Similarly, epichlorohydrin, allylglycidyl ether and phenyl glycidyl ether reacted with methanol affording excellent conversion (100%) and 90%, 90%, and 95% selectivity for product isomer C and 98%, 99%, and 98% selectivity for (C+D) in 20 min.

# 3.2.4. Plausible reaction pathway

When the epoxide molecule adsorbs to the ZrTf/S catalyst, acidic site is activated, which induces polarization causing electron deficiency on the highest substituted carbon of the epoxide ring (Scheme 3). The nucleophile (amine/alcohol) then attacks this electron deficient carbon followed by protonation of the epoxide O by a proton from the nucleophile to ultimately form the final product  $\beta$ -amino/ $\beta$ -alkoxy alcohol.

# 4. Conclusions

We have successfully demonstrated a general one-pot- twostep method for synthesis of metal triflate grafted mesoporous silica catalyst. The ZrTf/S catalyst prepared in the study was found to be easily synthesized, reusable and highly efficient for catalysis of epoxide ring opening by alcohols and amines. The ZrTf/S sample showed higher catalytic activity than the AlTf/S and TiTf/S samples owing to its higher acidity. Furthermore, high catalytic activity for epoxide ring opening with poor nucleophiles was obtained.

#### Acknowledgments

Authors are thankful to Chinese Academy of Sciences (CAS) and Dalian Institute of Chemical Physics, CAS for providing financial support and CAS President's International Fellowship Initiative funding.



We report the synthesis of zirconium triflate grafted mesoporous SBA-15 (ZrTf/S) using a simple one-pot-two-step synthesis. ZrTf/S showed excellent activity for ring opening of epoxides by various amines and alcohols under ambient conditions.

# References

- [1] O. Mitsunobu, in: E. Winterfeldt (ed.), *Comprehensive Organic Synthesis*, Pergamon Press, New York, **1996**, Part 1.3.4.1.
- [2] D. J. Ager, I. Prakash, D. R. Schaad, *Chem. Rev.*, **1996**, 96, 835–876.
- [3] E. J. Corey, F. Y. Zhang, Angew. Chem. Int. Ed., 1999, 38, 1931–1934.
- [4] P. O'Brien, Angew. Chem. Int. Ed., 1999, 38, 326-329.
- [5] G. G. Li, H. T. Chang, K. B. Sharpless, Angew. Chem. Int. Ed., 1996, 35, 451–454.
- [6] C. Baylon, G. Prestat, M. P. Heck, C. Mioskowski, *Tetrahedron Lett.*, 2000, 41, 3833–3835.
- [7] L. Saikia, J. K. Satyarthi, D. Srinivas, P. Ratnasamy, J. Catal., 2007, 252, 148–160.
- [8] R. I. Kureshy, S. Singh, N. H. Khana, S. H. R. Abdi, E. Suresh, R. V. Jasra, J. Mol. Catal. A, 2007, 264, 162–169.
- [9] D. Jiang, T. Mallat, F. Krumeich, A. Baiker, J. Catal., 2008, 257, 390–395.
- [10] M. W. C. Robinson, A. M. Davies, R. Buckle, I. Mabbett, S. H. Taylor, A. E. Graham, Org. Biomol. Chem., 2009, 7, 2559–2564.
- [11] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Chem. Eur. J., 2010, 16, 8530–8536.
- [12] F. Zaccheria, F. Santoro, R. Psaro, N. Ravasio, *Green Chem.*, 2011, 13, 545–548.
- [13] A. Kumar, D. Srinivas, J. Catal., 2012, 293, 126–140.
- [14] I. Matos, P. D. Neves, J. E. Castanheiro, E. Perez-Mayoral, R. Martin-Aranda, C. Duran-Valle, J. Vital, A. M. Botelho do Rego, I. M. Fonseca, *Appl. Catal. A*, **2012**, 439–440, 24–30.
- [15] M. Mirza-Aghayan, M. Alizadeh, M. Molaee. Tavana, R. Boukherroub, *Tetrahedron Lett.*, **2014**, 55, 6694–6697.
- [16] B. Tang, W. L. Dai, X. M. Sun, G. J. Wu, N. J. Guan, M. Hunger, L. D. Li, *Green Chem.*, **2015**, 17, 1744–1755.

- [17] S. Kobayashi, M. Sugiura, H. Kitagawa, W. W. L. Lam, Chem. Rev., 2002, 102, 2227–2302.
- [18] S. Kobayashi, K. Manabe, Acc. Chem. Res., 2002, 35, 209–217.
- [19] S. Kobayashi, Eur. J. Org. Chem., 1999, 15–27.
- [20] A. Kawada, S. Mitamura, S. Kobayashi, J. Chem. Soc., Chem. Commun., 1993, 1157–1158.
- [21] A. Kawada, S. Mitamura, S. Kobayashi, Chem. Commun., 1996, 183–184.
- [22] G. A. Olah, O. Farooq, S. M. F. Farnia, J. A. Olah, J. Am. Chem. Soc., 1988, 110, 2560–2565.
- [23] V. Sage, J. H. Clark, D. J. Macquarrie, J. Catal., 2004, 227, 502–511.
- [24] V. Sage, J. H. Clark, D. J. Macquarrie, J. Mol. Catal. A, 2003, 198, 349–358.
- [25] K. Mantri, K. Komura, Y. Kubota, Y. Sugi, J. Mol. Catal. A, 2005, 236, 168–175.
- [26] T. Kawabata, T. Mizugaki, K. Ebitani, K. Kaneda, J. Am. Chem. Soc., 2003, 125, 10486–10487.
- [27] C. Wiles, P. Watts, ChemSusChem, 2012, 5, 332–338.
- [28] S. Kobayashi, S. Nagayama, J. Org. Chem., 1996, 61, 2256-2257.
- [29] W. Q. Gu, W. J. Zhou, D. L. Gin, Chem. Mater., 2001, 13, 1949-1951.
- [30] B. M. Choudary, C. Sridhar, M. Sateesh, B. Sreedhar, J. Mol. Catal. A, 2004, 212, 237–243.
- [31] K. N. Tayade, M. Mishra, K. Munusamy, R. S. Somani, *Catal. Sci. Technol.*, **2015**, 5, 2427–2440.
- [32] A. Y. Khodakov, V. L. Zholobenko, R. Bechara, D. Durand, *Microporous Mesoporous Mater.*, 2005, 79, 29–39.
- [33] M. Chidambaram, C. Venkatesan, P. R. Rajamohanan, A. P. Singh, *Appl. Catal. A*, **2003**, 244, 27–37.
- [34] S. Selvakumar, N. M. Gupta, A. P. Singh, Appl. Catal. A, 2010, 372, 130–137.
- [35] D. H. Johnston, D. F. Shriver, Inorg. Chem., 1993, 32, 1045-1047.
- [36] A. Corma, V. Fornes, M. T. Navarro, J. Perez-pariente, J. Catal., 1994, 148, 569–574.

- [37] R. Mokaya, W. Jones, Z. Luan, M. D. Alba, J. Klinowski, *Catal. Lett.*, 1996, 37, 113–120.
- [38] A. Corma, Chem. Rev., **1995**, 95, 559–614.
- [39] A. Ramanathan, M. C. Castro Villalobos, C. Kwakernaak, S.

Telalovic, U. Hanefeld, *Chem. Eur. J.*, **2008**, 14, 961 – 972.

- [40] S. Y. Chen, J. F. Lee, S. Cheng, *J. Catal.*, **2010**, 270, 196–205.
- [41] R. Peng, D. Zhao, N. M. Dimitrijevic, T. Rajh, R. T. Koodali, J. Phys. Chem. C, 2012, 116, 1605–1613.