DOI: 10.1002/cctc.201402839

Preparation of Mesoporous Zeolite ETS-10 Catalysts for High-Yield Synthesis of α,β-Epoxy Ketones

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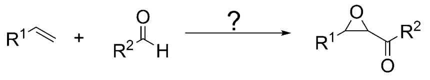
Developing highly active heterogeneous catalysts for the efficient construction of valuable building blocks is of great importance to synthetic chemistry. For this purpose, a mesoporous zeolite ETS-10 (METS-10) is synthesized by using a mesoscale silane surfactant as a template and applied to achieve highly efficient syntheses of α,β-epoxy ketones by employing simple alkenes and aldehydes as starting materials. The high activity of the METS-10 catalyst is attributed to its unique porous structure and basicity. Electron paramagnetic resonance characterization results and theoretical calculation experimental data reveal that the strong basic sites on METS-10 catalyst can activate the reaction substrate and intermediate. In addition, the mesopores in METS-10 catalyst benefit the mass transfer and further improve the catalytic activity.

α,β-Epoxy ketones are crucial intermediates and precursors for chemical transformations to many natural products and drug molecules.[1] A variety of synthetic approaches have been developed for the preparation of this class of compounds.[2–4] However, until now almost all the successful syntheses of α,β-epoxy ketones have been a two-step procedure that involves workup: synthesis of α,β-unsaturated ketones, followed by the epoxidation of α,β-unsaturated ketones with hydroperoxides under alkaline conditions.[5] Recently, Liu et al. revealed that the oxidative coupling of aldehyde C sp^2–H bonds with alkenes in the presence of iron salts furnishes β-peroxy ketones that can be transformed further into the corresponding epoxides in the presence of organic base.[6] However, besides the economic considerations for these complex synthetic routes, the isolation of the employed metal salts and organic amines from the reaction mixture is also difficult. Therefore, developing highly efficient heterogeneous catalysts for the direct construction of these types of compounds by employing simple alkenes and aldehydes as starting materials is very desirable (Scheme 1).



Scheme 1. Direct synthesis of α,β-epoxy ketones.

It is well known that bases are usually crucial for the epoxidation of α,β-unsaturated carbonyl compounds.[2] Thus, developing a porous heterogeneous catalyst with the required basic properties may provide a facile access to α,β-epoxy ketones. Associated studies have reported that the titanosilicate zeolite ETS-10 has a three-dimensional 12-membered ring network and possesses strong basicity.[7] The basic characteristic is closely related to its unique framework that comprises corner-sharing TiO_6^{2-} octahedra and SiO_4 tetrahedra as building units, in which each TiO_6 unit contributes two negative charges that are compensated by extra-framework cations.[7a] Such framework architectures and chemical compositions should be envisioned to present a unique catalytic performance in synthetic chemistry.

Based on fundamentals discussed above, we synthesized mesoporous zeolite ETS-10 (METS-10) by templating with a mesoscale silane surfactant and applied it to the direct transformation of alkenes and aldehydes to α,β-epoxy ketones. For comparison, mesopore-free ETS-10, mesoporous NaX (MX), mesoporous TS-1 (MTS-1), and mesoporous Fe-doped ZSM-5 (Fe-MZSM-5) zeolites were also synthesized (see Section 1 in the Supporting Information). Compared with MX, MTS-1, and Fe-MZSM-5, the strong basic METS-10 catalysts exhibited high activity for the synthesis of α,β-epoxy ketones. The reason for the high catalytic activity of METS-10 catalysts in this transformation was studied fully by using the electron paramagnetic resonance technique (EPR) and DFT theoretical calculations.

XRD patterns, N_2 isotherms, SEM and TEM images of METS-10, and IR and magic-angle spinning NMR spectra of the catalysts with adsorbed pyrrole are shown in Figure 1. The XRD patterns of the ETS-10 zeolite structure give well-resolved

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201402839.

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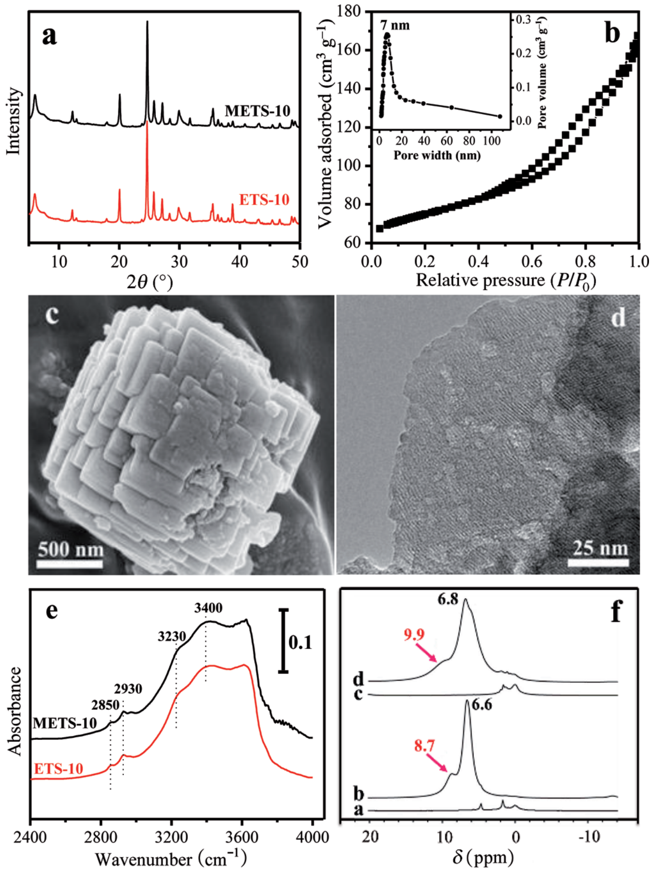
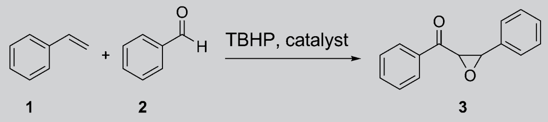


Figure 1. a) XRD patterns of METS-10 and ETS-10. b) N_2 adsorption isotherms of METS-10. c) SEM image of METS-10. d) TEM image of thin-sectioned METS-10. e) IR spectra of pyrrole adsorbed on METS-10 and ETS-10 outgassed at 100 °C. f) ^1H magic-angle spinning NMR spectra of METS-10 and MX zeolites before and after the adsorption of pyrrole, respectively: a, b: MX, c, d: METS-10.

peaks in the 5–50° range (Figure 1 a).[7a] The N_2 isotherms of METS-10 exhibit a step at a relative pressure of 0.5–0.9, which is assigned to the presence of mesopores (Figure 1 b). Correspondingly, the mesopore size distribution is centered at 7 nm (Figure 1 b, insert). Sample textual parameters are presented in Table S1. The SEM images reveal METS-10 to have similar morphologies to ETS-10 and particle sizes of 1–1.5 μm (Figure 1 c and Figure S1). The light areas in the TEM image of the thin-sectioned sample represent mesoporous cavities within the crystals (Figure 1 d). The size range of the mesopores determined by TEM analysis is 6–8 nm, which is in good agreement with the pore size distribution derived from N_2 sorption experiments (insert in Figure 1 b). To characterize the basicity of catalysts, pyrrole adsorption was studied by using IR spectroscopy. As shown in Figure 1 e, the NH stretching bands at $\tilde{\nu}=3200$–$3400\ cm^{-1}$ are attributed to the interactions between pyrrole species and the basic sites.[8] The characteristic peaks of N–H stretching at $\tilde{\nu}=3400$ and $3230\ cm^{-1}$ combined with the bands at $\tilde{\nu}=2930$ and $2850\ cm^{-1}$ reveal the basic sites on the surface of METS-10 and ETS-10. The intrinsic basicity of METS-10 was investigated further by NMR spectroscopy of pyrrole adsorption experiments and was compared to basic zeolite MX. Commonly, the ^1H peak of the N–H bond in liquid pyrrole appears at 7.1 ppm and shifts to higher frequency if adsorbed on basic sites. It has been shown that a lower field ^1H chemical shift can indicate a stronger basicity of the samples.[9] In Figure 1 f, the characteristic peak is shifted to 9.9 ppm for METS-10 and 8.7 ppm for MX after the adsorption of pyrrole, which unambiguously suggests that the basicity of zeolite METS-10 is stronger than that of MX.

The direct coupling of alkenes with aldehydes to synthesize α,β-epoxy ketones was studied firstly by using styrene and benzaldehyde as the model substrates to investigate our tentative idea that the strong basic METS-10 catalyst can provide facile access to α,β-epoxy ketones and should present a unique catalytic performance under different reaction conditions (Table 1). To our delight, the desired α,β-epoxy ketone was obtained in high product yield (98 %) by using basic METS-10 as catalyst (entry 1). The mesopore-free ETS-10 catalyst gave a much lower yield of 82 % (entry 2). This difference was attributed to the mesoporosity of zeolite ETS-10 facilitating the mass transfer and thus improving the catalytic activity. Compared with METS-10, the MX had a relatively high mesoporous surface area (130 $m^2\,g^{-1}$, Table S1) but still showed a relatively low catalytic activity (entry 3), which could be attributed to its relatively weaker basicity. In addition, the relatively neutral mesoporous zeolite MTS-1 and the Fe-containing mesoporous zeolite Fe-MZSM-5 were inactive (entries 4 and 5). These results suggested that the Ti species in zeolite and the Fe metal catalyst did not catalyze this epoxidation reaction. Notably, the epoxide product was formed in moderate yields by using inorganic alkali salt catalysts (entries 6–8). However, in a reaction mixture without basic catalyst, the desired product was not obtained, even after prolonging the reaction time and enhancing the reaction temperature (entries 9 and 10).

Table 1. Synthesis of α,β-epoxy ketone over a series of catalysts under different conditions.[a]



Entry	Catalyst	*T* [°C]	*t* [h]	Yield [%][b]
1	METS-10	90	10	98 (94)[c]
2	ETS-10	90	10	82 (77)[c]
3	MX	90	10	75 (70)[c]
4	MTS-1	90	10	-
5	Fe-MZSM-5	90	10	-
6	K_2CO_3[d]	90	10	64
7	Na_2CO_3[d]	90	10	62
8	Cs_2CO_3[d]	90	10	65
9	–	90	15	–
10	–	110	10	–

[a] Reaction conditions: styrene (0.5 mmol), benzaldehyde (1.0 mmol), TBHP (1.0 mmol, 70 % aqueous solution), catalyst (40 mg), MeCN (2.0 mL). [b] Obtained by GC analysis. [c] Isolated yield in parenthesis. [d] A molar equivalent of alkali equal to 40 mg METS-10 was used.

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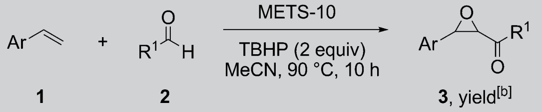
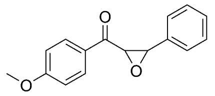
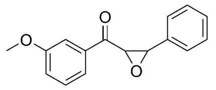
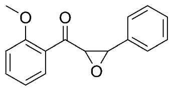
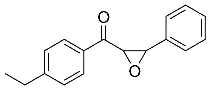
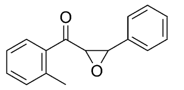
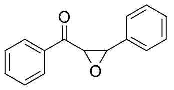
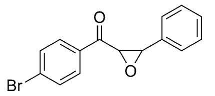
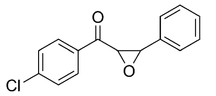
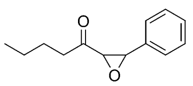
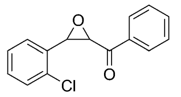
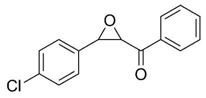
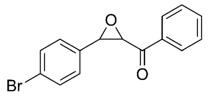
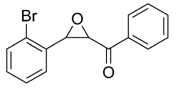
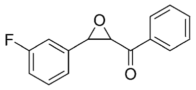
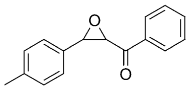
Table 2. Synthesis of α,β-epoxy ketone from various aldehydes with substituted styrenes.[a]



 **3a**, 96 (91)%	 **3b**, 95 (90)%	 **3c**, 95 (90)%
 **3d**, 94 (91)%	 **3e**, 96 (91)%	 **3f**, 98 (94)%
 **3g**, 93 (88)%	 **3h**, 96 (91)%	 **3i**, 89 (82)%
 **3j**, 95 (91)%	 **3k**, 96 (90)%	 **3l**, 97 (92)%
 **3m**, 94 (90)%	 **3n**, 96 (91)%	 **3o**, 93 (88)%

[a] Conditions: 1 (0.5 mmol), 2 (1.0 mmol), TBHP (1.0 mmol), METS-10 (40 mg), MeCN (2.0 mL), 90 °C, 10 h. [b] Obtained by GC analysis; isolated yields given in parentheses.

Encouraged by the above promising results, we went on to study a series of substrates in the METS-10-catalyzed oxidative coupling of alkenes with aldehydes (Table 2). First, the scope of the aldehyde substrate was investigated. The use of benzaldehyde with an easily oxidisable methoxyl substituent afforded the desired product (**3a**–**3c**) in good yields. *para*-Ethyl and *ortho*-methyl substituted benzaldehydes were also found to be suitable substrates for this transformation, forming the corresponding α,β-epoxy ketones (**3d** and **3e**) in excellent yields. A carbon–halogen bond, which provided the possibility for further functionalization of the products (**3g** and **3h**), was tolerated well in this transformation. Furthermore, aliphatic aldehyde was applied to this transform to produce a good yield of **3i**. The scope of substituted styrene was examined next. Styrene with halogen substituents at the *para* and *ortho* positions as electron-withdrawing groups afforded the desired products in excellent yields (**3j**–**3n**). Notably, methyl substituents on the phenyl ring of styrene were also tolerated well, affording the desired products in good yield (**3o**). The reusability of METS-10 catalyst was also surveyed. After the reaction, the catalyst was separated simply by filtration and washed with ethanol, dried at 120 °C for 10 h, and reused 6 times with almost no loss of the activity (Table S2). These results indicated that the METS-10 catalyst had a good catalyst life, one of the key features in the application of industrial catalysts.

To shed light on the reaction mechanism of the METS-10-catalyzed oxidative coupling reactions, radical-trapping experiments were investigated by EPR analysis. In EPR analysis of the reaction mixture of phenyl-*N*-*tert*-butylnitrone (PBN) and CH_3CN with and without METS-10 catalyst at 70 °C, no signal was observed (Figure 2a and b). In contrast, in EPR analysis of the reaction mixture of PBN, CH_3CN, and *tert*-butyl hydroperoxide (TBHP) in the absence of METS-10 catalyst, the strong signal of alkyloxy radical (tBuO$^•$) generated from TBHP in the reaction mixture was observed (Figure 2c).[10] Very importantly, for the reaction mixture of PBN, CH_3CN, and TBHP in the presence of the basic METS-10 catalyst, not only the alkyloxy radical signal but also the alkylperoxy radical (tBuOO$^•$) signal[10] (indicated by red square in Figure 2d) were observed. Our theoretical calculation illustrated that the dissociation energies of TBHP to form tBuO$^•$ and tBuOO$^•$ were 48.7 and 85.4 kcal mol^{-1} (see Section 7 in the Supporting Information), respectively. Apparently, the formation of tBuOO$^•$ is more difficult than that of tBuO$^•$. However, the strong basicity of METS-10 facilitates the tBuOO$^•$ formation, as shown in EPR experimental results (Figure 2d). The theoretical calculation results also illustrated that the dissociation energies of TBHP to tBuOO$^•$ decreased from 85.4 to 66.9 kcal mol^{-1} in the presence of the strongly basic zeolite METS-10 (see Section 7 in the Supporting Information). These results suggested that the basic METS-10 catalyst played a critical role in the generation of tBuOO$^•$, which was proposed to be the key intermediate for the formation of α,β-epoxy ketone (see the proposed mechanism in Scheme 2).

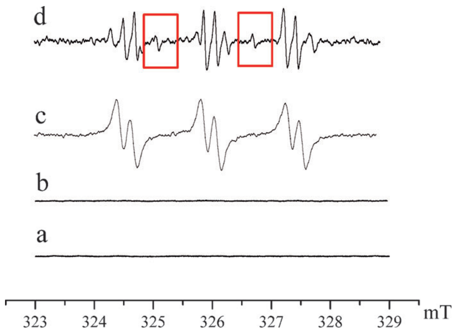


Figure 2. EPR spectra of a series of reaction mixtures at 70 °C: a) PBN and CH_3CN; b) METS-10 catalyst, PBN, and CH_3CN; c) PBN, CH_3CN, and TBHP; and d) METS-10 catalyst, PBN, CH_3CN, and TBHP.

To examine the possible organic radical intermediates, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added to the reaction system (see Section 6 in the Supporting Information). As a result, TEMPO-adduct aldehyde product **4** was obtained instead of α,β-epoxy ketone **3** (Scheme 3). These results demonstrated that acyl radical was generated from the abstraction of the aldehydic hydrogen by the alkyloxy radical under the reaction conditions.

Based on the above results, literature reports,[6,11] and the basicity of ETS-10,[7] a reaction pathway was proposed (Scheme 2). It is suggested that tBuOOH is readily split into alkyloxy and alkylperoxy radicals by facilitation of the basic sites

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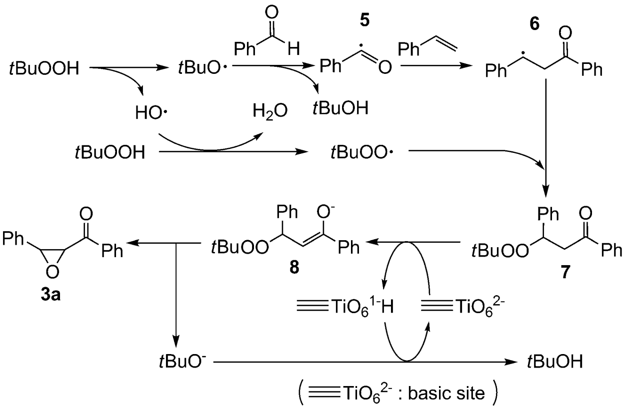
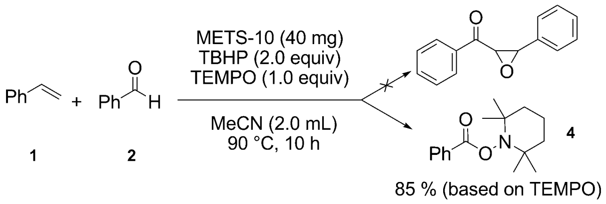


Scheme 2. Proposed mechanism.



Scheme 3. Investigation of the reaction mechanism.

(marked as $\equiv TiO_6^{2-}$) on the METS-10 catalyst under heating. In this manner, aldehydic hydrogen is abstracted by alkyloxy radical to yield acyl radical **5**.[12] The radical addition of **5** to alkene gives the benzylic radical **6**, followed by radical coupling with alkylperoxy leading to the intermediate β-peroxy ketone **7**.[6,13] The α-hydrogen in the β-peroxy ketone **7** can be easily abstracted by basic sites ($\equiv TiO_6^{2-}$) on METS-10 to form a hydroperoxide enolate **8**, which is followed by loss of the alkyloxy group in concomitant ring closure and formation of the epoxide **3a**.[2b,4a–c]

DFT theoretical calculations have been used extensively in the mechanistic studies of both heterogeneous and homogeneous catalytic reactions. To reveal the epoxide **3a** formation mechanism, the pathways were investigated in detail by theoretical calculation at the ωB97XD/6-31G(d,p) level (see Section **7** in the Supporting Information). This illustrated that the formation of intermediates (**5**, **6**, and **7** in Scheme 2) involving radicals was almost barrier-free. The structures of **8** and according epoxidation transition states are shown in Figure 3. In the transition state, the C1–O1 bond distance decreased to 1.820 Å, significantly shorter than that in the reactant **8** (2.362 Å), suggesting that the three-membered ring C2–C1–O1 would be formed. Simultaneously, the O1–O2 bond length was elongated to 1.987 Å from 1.447 Å in reactant **8**, which was indicative of the dissociation of O1–O2 bond and the release of *t*BuO⁻ anion, which was then re-bound to the acidic proton on the ETS-10 framework to result in the generation of *t*BuOH. Furthermore, the activation energy barrier of this step was 17.34 kcal mol^{-1} based on the optimized structures. Such a low barrier demonstrated the possibility of formation of **3a**.

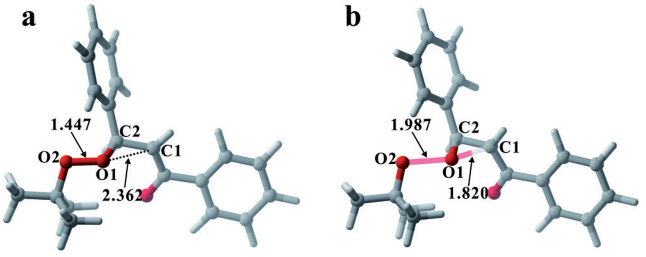


Figure 3. Optimized geometries of a) reactant **7** and b) its transition state for epoxide **3a** formation. Selected interatomic distances are indicated in [Å].

Conclusions

Mesoporous zeolite ETS-10 was synthesized by using a mesoscale silane surfactant as a template and applied to the direct synthesis of α,β-epoxy ketones through the oxidative coupling of alkenes and aldehydes. A variety of functional groups on both the aldehyde and alkene substrates were well-tolerated. The strong basic sites on METS-10 catalyst facilitated the activation of the reaction substrate and intermediate, resulting in the observed high catalytic activity. In addition, mesopores in METS-10 benefitted the mass transfer and therefore improved its catalytic performance.

Experimental Section

Synthesis of METS-10 and mesopore-free ETS-10

METS-10 was synthesized hydrothermally from a titanosilicate gel with a molar composition $4.4\,Na_2O/1.9\,K_2O/1.0\,TiO_2/7.1\,SiO_2/0.65\,TPOAB/0.39\,Hacac/163.0\,H_2O$ (TPOAB: mesoscale template of *N*,*N*-dimethyl-*N*-octadecyl-*N*-(3-triethoxysilylpropyl) ammonium bromide; Hacac: acetylacetonate). In a typical run, 6.25 м aqueous NaOH (3.0 mL) was mixed with aqueous waterglass solution (SiO_2/Na_2O molar ratio: 3.67, 4.84 mL) under vigorous stirring and the obtained solution was denoted solution A. Hacac (0.3 g) was added to $TiCl_3$ solution (3.5 g, 17 wt% in HCl) and stirred for 20 min, followed by slow dropwise addition to solution A under stirring for 60 min. Then, 3.75 м KF aqueous solution (4.0 mL) was added, followed by addition of TPOAB (1.5 mL). After further stirring for 2 h, the obtained gel was transferred into a Teflon-coated stainless-steel autoclave for crystallization at 230 °C for 72 h. The resulting product was filtered, washed, and dried at 100 °C overnight and calcined in air at 450 °C for 5 h. For comparison, mesopore-free ETS-10 zeolite was synthesized by the same procedure, with the exception of the addition of TPOAB and Hacac.

Synthesis of α,β-epoxy ketones

General procedure: METS-10 (40 mg) was added to a Schlenk tube equipped with a magnetic stirrer bar. Styrene (0.5 mmol), benzaldehyde (2 equiv, 1 mmol), and TBHP (1.0 mmol, 70% aqueous solution) were injected into the reaction tube. The reaction mixture was then heated to 90 °C and stirred for 10 h. Once the reaction was finished, the catalyst was separated by centrifugation and filtering to obtain the liquid phase. The liquid products were analyzed with an Agilent 7890A GC equipped with a flame ionization detector. The pure product was obtained by flash column chromatography on silica gel (petroleum/ethyl acetate = 100:1). ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded at 20 °C with $CDCl_3$ as the solvent. Chemical shifts were reported relative to the internal standard TMS at RT.

Further details of material characterizations and syntheses are given in the Supporting Information.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21173255, U162115, and 21476030) and the Natural Science Foundation of Zhejiang Province of China (Z14B060012).

Keywords: aldehydes · epoxidation · mesoporous materials · ketones · zeolites

[1] a) W. Adam, C. R. Saha-Möller, P. A. Ganeshpure, *Chem. Rev.* **2001**, *101*, 3499–3548; b) P. I. Dalko, L. Moisan, *Angew. Chem. Int. Ed.* **2004**, *43*, 5138–5175; *Angew. Chem.* **2004**, *116*, 5248–5286; c) Q. Xia, H. Ge, C. Ye, Z. Liu, K. Su, *Chem. Rev.* **2005**, *105*, 1603–1662; d) D. E. Bergbreiter, J. Tian, C. Hongfa, *Chem. Rev.* **2009**, *109*, 530–582; e) M. J. Climent, A. Corma, S. Iborra, *Chem. Rev.* **2011**, *111*, 1072–1133.

[2] For amine-catalyzed epoxidations of α,β-unsaturated carbonyl compounds, see: a) M. Marigo, J. Franzén, T. B. Poulsen, W. Zhuang, K. A. Jørgensen, *J. Am. Chem. Soc.* **2005**, *127*, 6964–6965; b) X. Lu, Y. Liu, B. Sun, B. Cindric, L. Deng, *J. Am. Chem. Soc.* **2008**, *130*, 8134–8135; c) A. Lattanzi, *Chem. Commun.* **2009**, 1452–1463; d) J. Li, N. Fu, L. Zhang, P. Zhou, S. Luo, J. Cheng, *Eur. J. Org. Chem.* **2010**, 6840–6849; e) O. Lifchits, C. M. Reisinger, B. List, *J. Am. Chem. Soc.* **2010**, *132*, 10227–10229; f) R. A. Miranda, J. Llorca, F. Medina, J. E. Sueiras, A. M. Segarra, *J. Catal.* **2011**, *282*, 65–73; g) Y. Demizu, N. Yamagata, S. Nagoya, Y. Sato, M. Doi, M. Tanaka, K. Nagasawa, H. Okuda, M. Kurihara, *Tetrahedron* **2011**, *67*, 6155–6165; h) O. Lifchits, M. Mahlau, C. M. Reisinger, A. Lee, C. Farès, I. Polyak, G. Gopakumar, W. Thiel, B. List, *J. Am. Chem. Soc.* **2013**, *135*, 6677–6693.

[3] For transition metal complex-catalyzed epoxidation of α,β-unsaturated carbonyl compounds, see: a) E. A. Prasetyanto, N. H. Khan, H. U. Seo, S. E. Park, *Top Catal.* **2010**, *53*, 1381–1386; b) Y. Chu, X. Liu, W. Li, X. Hu, L. Lin, X. Feng, *Chem. Sci.* **2012**, *3*, 1996–2000; c) W. Dai, J. Li, G. Li, H. Yang, L. Wang, S. Gao, *Org. Lett.* **2013**, *15*, 4138–4141; d) S. A. Hauser, M. Cokoja, F. E. Ku, *Catal. Sci. Technol.* **2013**, *3*, 552–561; e) N. C. Maity, P. K. Bera, D. Ghosh, S. H. R. Abdi, R. I. Kureshy, N. H. Khan, H. C. Bajaj, E. Suresh, *Catal. Sci. Technol.* **2014**, *4*, 208–217.

[4] a) I. López, S. Rodríguez, J. Izquierdo, F. V. González, *J. Org. Chem.* **2007**, *72*, 6614–6617; b) H. Jin, H. Zhao, F. Zhao, S. Li, W. Liu, G. Zhou, K. Tao, T. Hou, *Ultrason. Sonochem.* **2009**, *16*, 304–307; c) W. W. Leung, R. M. Savizky, *Ind. Eng. Chem. Res.* **2010**, *49*, 12327–12330; d) J. M. Fraile, N. García, C. I. Herrerías, J. A. Mayoral, *Catal. Today* **2011**, *173*, 15–20.

[5] a) B. M. Choudary, M. L. Kantam, K. V. S. Ranganath, K. Mahendar, B. Sreedhar, *J. Am. Chem. Soc.* **2004**, *126*, 3396–3397; b) Y. G. Wang, J. X. Ye, X. M. Liang, *Adv. Synth. Catal.* **2007**, *349*, 1033–1036; c) W. Luo, Z. Yu, W. Qiu, F. Yang, X. Liu, J. Tang, *Tetrahedron* **2011**, *67*, 5289–5292.

[6] W. Liu, Y. Li, K. Liu, Z. Li, *J. Am. Chem. Soc.* **2011**, *133*, 10756–10759.

[7] a) M. W. Anderson, O. Terasaki, T. Ohsuna, A. Philippou, S. P. MacKay, A. Ferreira, J. Rocha, S. Lidin, *Nature* **1994**, *367*, 347–351; b) M. E. Grillo, J. Carrazza, *J. Phys. Chem.* **1996**, *100*, 12261–12264; c) X. Wang, A. J. Jacobson, *Chem. Commun.* **1999**, 973–974; d) X. Yang, J. L. Pallaud, H. F. W. J. van Breukelen, H. Kessler, E. Duprey, *Microporous Mesoporous Mater.* **2001**, *46*, 1–11; e) S. B. Waghmode, R. Vetrivel, S. G. Hegde, C. S. Gopinath, S. Sivasanker, *J. Phys. Chem. B* **2003**, *107*, 8517–8523; f) J. Li, B. Shen, Q. Guo, W. Zhang, G. Wen, R. Tian, Z. Zhang, *Microporous Mesoporous Mater.* **2011**, *145*, 224–230.

[8] a) J. Xie, M. Huang, S. Kaliaguine, *Catal. Lett.* **1994**, *29*, 281–291; b) P. O. Scokart, P. G. Rouxhet, *Bull. Soc. Chim. Belge.* **1981**, *90*, 983–984.

[9] M. Sánchez-Sánchez, T. Blasco, *Chem. Commun.* **2000**, 491–492.

[10] E. Niki, S. Yokoi, J. Tsuchiya, Y. Kamiya, *J. Am. Chem. Soc.* **1983**, *105*, 1498–1503.

[11] a) J. Kim, R. G. Harrison, C. Kim, L. Que, Jr., *J. Am. Chem. Soc.* **1996**, *118*, 4373–4379; b) P. A. MacFaul, D. D. M. Wayner, K. U. Ingold, *Acc. Chem. Res.* **1998**, *31*, 159–162; c) D. H. R. Barton, *Tetrahedron* **1998**, *54*, 5805–5817; d) P. Stavropoulos, R. Celenligil-Cetin, A. E. Tapper, *Acc. Chem. Res.* **2001**, *34*, 745–752; e) K. Liu, Y. Li, X. Zheng, W. Liu, Z. Li, *Tetrahedron* **2012**, *68*, 10333–10337.

[12] a) C. Chatgilialoglu, D. Crich, M. Komatsu, I. Ryu, *Chem. Rev.* **1999**, *99*, 1991–2069; b) C. Chan, Z. Zhou, A. S. C. Chan, W. Yu, *Org. Lett.* **2010**, *12*, 3926–3929; c) B. Tang, R. Song, C. Wu, Y. Liu, M. Zhou, W. Wei, G. Deng, D. Yin, J. Li, *J. Am. Chem. Soc.* **2010**, *132*, 8900–8902; d) Y. Wu, B. Li, F. Mao, X. Li, F. Y. Kwong, *Org. Lett.* **2011**, *13*, 3258–3261; e) C. Li, L. Wang, P. Li, W. Zhou, *Chem. Eur. J.* **2011**, *17*, 10208–10212.

[13] a) A. Bravo, H. R. Bjørsvik, F. Fontana, L. Liguori, F. J. Minisci, *J. Org. Chem.* **1997**, *62*, 3849–3857; b) A. Studer, *Chem. Eur. J.* **2001**, *7*, 1159–1164; c) A. Studer, *Chem. Soc. Rev.* **2004**, *33*, 267–273; d) A. Studer, T. Schulte, *Chem. Rec.* **2005**, *5*, 27–35.

Received: October 20, 2014
Revised: November 16, 2014
Published online on ■■ ■■, 0000

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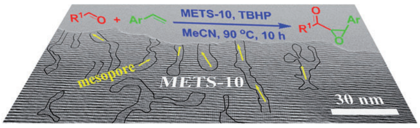
Preparation of Mesoporous Zeolite ETS-10 Catalysts for High-Yield Synthesis of α,β-Epoxy Ketones



Mesoporous zeolite ETS-10 is synthesized by using mesoscale silane surfactant as a template and applied to the highly efficient synthesis of α,β-epoxy ketones by employing simple alkenes and aldehydes as starting materials. The high activity of the mesoporous ETS-10 catalyst is attributed to its unique porous structure and basicity. The TiO_6^{2-} octahedral unit in ETS-10 framework is strongly basic, activating the reaction substrate and intermediate to give high catalytic activity. Mesopores in the ETS-10 aid mass transfer, enhancing the catalytic performance further.

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