# ARTICLE IN PRESS

# Tetrahedron xxx (2013) 1-5

Contents lists available at SciVerse ScienceDirect

# Tetrahedron



journal homepage: www.elsevier.com/locate/tet

# An efficient and scalable room temperature aerobic alcohol oxidation catalyzed by iron chloride hexahydrate/mesoporous silica supported TEMPO

Lianyue Wang<sup>a</sup>, Jun Li<sup>a</sup>, Xiaoping Zhao<sup>b</sup>, Ying Lv<sup>a</sup>, Hengyun Zhang<sup>a</sup>, Shuang Gao<sup>a,\*</sup>

<sup>a</sup> Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, DNL, Dalian 116023,

People's Republic of China <sup>b</sup> Shaanxi Yanchang Petroleum (Group) Co., Ltd., Xi'an 716000, People's Republic of China

# ARTICLE INFO

Article history: Received 8 April 2013 Accepted 20 May 2013 Available online xxx

Keywords: Alcohol oxidation Iron chloride Molecular oxygen 2,2,6,6-Tetramethylpiperidine N-Oxyl (TEMPO) SBA-15

# ABSTRACT

An efficient room temperature catalytic system FeCl<sub>3</sub>· $6H_2O/SBA-15$ -TEMPO/NaNO<sub>2</sub> for the oxidation of alcohols with dioxygen or air as terminal oxidant has been developed. Various alcohols were oxidized at a low catalyst loading (0.1–1 mol %) to the corresponding carbonyl compounds in good to excellent yields. For the oxidation of benzyl alcohol, the excellent turn-over frequency (TOF) of 81.4  $h^{-1}$  was achieved (turn-over number (TON) up to 9770). The catalyst SBA-15-TEMPO can be reused for 10 reaction runs without significant loss of catalytic activity. In addition, the two components FeCl<sub>3</sub>· $6H_2O$  and SBA-15-TEMPO can also be reused for at least four reaction runs without appreciable loss of catalytic activity. In the case of large-scale experiment for the oxidation of benzyl alcohol, the desired product benzal-dehyde was obtained in 94.5% yield.

© 2013 Elsevier Ltd. All rights reserved.

# 1. Introduction

The selective oxidation of alcohols into the corresponding carbonyl compounds is one of the most important transformations in organic chemistry, and the carbonyl compounds are used in production of bulk and fine chemicals such as perfumes, pharmaceuticals and organic intermediates.<sup>1</sup> Traditional methods for this transformation are the use of stoichiometric oxidants such as MnO<sub>2</sub>, chromium salts, and the Dess–Martin reagent, which produce large amounts of unwanted toxic waste.<sup>2</sup> From both economic and environmental viewpoints, molecular oxygen, as a green oxidant, has received intensive attention because dioxygen is inexpensive and water is produced as the only byproduct. Many catalytic systems have been shown to be capable of catalyzing alcohol oxidation to the corresponding aldehydes and ketones with molecular oxygen.<sup>3</sup> Of particular interest in this field is the use of stable nitroxyl radical 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) as catalyst. Systems involving TEMPO as catalyst in combination with metal or metal-free co-catalysts and molecular oxygen as terminal oxidant for the oxidation of alcohols have been reported.<sup>4</sup> Although these systems have been shown high efficiency for the alcohol oxidation, some limitations still exist with these systems. TEMPO is an expensive chemical reagent. Recovery and recycling of the homogeneous TEMPO is difficulty. The process of its separation from the product is troublesome. TEMPO residues in the product will affect the purity of the product. To address some of these limitations, heterogenization of homogeneous catalysts on solid supports shows high potential advantages, such as easy separation, efficient recycling of the supported catalyst.<sup>5</sup>

There have been many reports on the immobilization of TEMPO onto either organic<sup>6</sup> or inorganic supports.<sup>7</sup> These supported TEMPO catalysts were employed in the oxidation of alcohols under Anelli's and Minisci's conditions.<sup>8</sup> In Minisci conditions AcOH was used as a solvent, which was not favourable to the substrates containing acid-sensitive functional groups. In addition, the amount of the supported TEMPO was used up to 10 mol %. Quite recently, Karimi reported a heterogeneous catalytic system consisting of SBA-15-supported TEMPO/Bu<sub>4</sub>NBr/NaNO<sub>2</sub> for the oxidation of alcohols at 50–60 °C.<sup>9</sup> While the low loading of supported TEMPO (1–1.5 mol %) was used, the acidic solvent was used and the toxic and corrosive Br<sub>2</sub> was generated in situ. To our knowledge, very few catalytic systems have the advantages of using low catalytic amount of recyclable supported TEMPO catalyst for the oxidation of alcohols with dioxygen or air as terminal oxidant at room

<sup>\*</sup> Corresponding author. Tel./fax: +86 (0) 411 84379728; e-mail address: sgao@ dicp.ac.cn (S. Gao).

<sup>0040-4020/\$ –</sup> see front matter @ 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.tet.2013.05.076

# **ARTICLE IN PRESS**

L. Wang et al. / Tetrahedron xxx (2013) 1-5

temperature. Therefore, the development of highly efficient and reusable catalytic system for the aerobic alcohol oxidation under mild conditions (room temperature and little catalyst) should attract a great deal of attention from the viewpoint of green and sustainable chemistry. Liang has reported that FeCl<sub>3</sub>/TEMPO/NaNO<sub>2</sub> catalytic system is capable of selective oxidizing various alcohols with air as oxidant at room temperature.<sup>4f,h</sup> While this method provided a very mild reaction condition and obtained great achievement in the aerobic alcohol oxidation, the amount of the homogeneous, non-recyclable TEMPO was needed up to 5 mol %, which made this route less attractive for practical purposes.

The ordered mesoporous silica based materials as well-defined catalyst support has aroused great interest for researchers due to their uniform pore distribution, large void volumes, high surface areas and high hydrothermal stability.<sup>10</sup> Compared with amorphous solids and organic polymers, the ordered mesoporous silicas possibly provide a more comfortable environment for the interaction between catalysts and substrates. We selected a representative mesoporous material SBA-15 as support for TEMPO due to its obvious advantages mentioned above. It has been well documented that SBA-15 proved to be an excellent support for immobilizing organocatalysts or metal nanoparticles.<sup>11</sup> Herein, we reported an efficient room temperature oxidation of alcohols catalytic system by using a low catalytic amount of SBA-15-supported TEMPO in conjugation with FeCl<sub>3</sub>·6H<sub>2</sub>O/NaNO<sub>2</sub> co-catalysts with dioxygen or air as terminal oxidant.

# 2. Results and discussion

The catalyst was prepared from amine-grafted SBA-15 by coupling with 4-oxo-TEMPO through reductive amination. SBA-15 was obtained using pluronic 123 ( $EO_{20}PO_{70}EO_{20}$ , EO=ethylene oxide, PO=propylene oxide,  $M_w$ =5800) as the structure-directing template and tetraethoxysilane (TEOS) as silica precursor under acidic conditions following the well-known procedure.<sup>12</sup> The amine-functionalized SBA-15 (SBA-15–NH<sub>2</sub>) was prepared by the post-synthesis grafting process using 3-aminopropyltrimethoxysilane in refluxing dry toluene.<sup>9a</sup> The loading of amine was determined to be 0.30 mmol g-1 by elemental analysis. The resulting SBA-15–NH<sub>2</sub> was then reacted with methanol solution of 4-oxo-TEMPO to afford the grafting of TEMPO catalyst SBA-15-TEMPO.<sup>9a</sup> The unreacted and adsorbed species were removed by thorough washing with hot methanol using a Soxhlet apparatus. The loading of TEMPO was determined to be 0.21 mmol g<sup>-1</sup> by elemental analysis.

 $N_2$  adsorption–desorption and XRD were used to characterize the structure of SBA-15 and SBA-15-TEMPO. The  $N_2$  sorption isotherms of the corresponding SBA-15 and SBA-15-TEMPO are shown in Fig. 1. Both exhibit typical type-IV isotherm pattern with a sharp hysteresis loop, which is characteristic of the ordered mesoporous materials with narrow pore size distribution. Total pore volume was obtained from the volume of  $N_2$  adsorbed at  $P/P_0=0.95$ . Pore diameter was calculated using the BJH model based on the adsorption branch of the isotherms. SBA-15 has a BET surface area of 510 m<sup>2</sup> g<sup>-1</sup>, a regular pore diameter of 9.48 nm and a total pore volume of 0.93 cm<sup>3</sup> g<sup>-1</sup>. Compared with the parent material SBA-15, SBA-15-TEMPO has a lower surface area of 432 m<sup>2</sup> g<sup>-1</sup>, a smaller regular pore diameter of 7.68 nm and a total pore volume of 0.80 cm<sup>3</sup> g<sup>-1</sup>. These results may support a fact that organic moieties were introduced into the silica channels.

Powder X-ray diffraction patterns of SBA-15 and SBA-15-TEMPO are shown in Fig. 2. Both consist of three characteristic XRD peaks in the range  $2\theta$ <10°. They are typical for SBA-15-type hexagonal mesoporous molecular sieves. SBA-15-TEMPO shows slightly lower diffraction intensity compared to the parent material SBA-15, also indicating that the organic moieties exist in the mesopores. TEM images of SBA-15 and SBA-15-TEMPO further confirmed their



Fig. 1. N<sub>2</sub> sorption isotherms of SBA-15 (a) and SBA-15-TEMPO (b).



Fig. 2. XRD patterns of SBA-15 (a) and SBA-15-TEMPO (b).

well-ordered mesoporous structure. It was also verified that the porous structure was not changed after the post-grafting synthesis.

We examined the catalytic oxidation of benzyl alcohol with SBA-15-TEMPO catalyst and the results are shown in Table 1. The reaction proceeded using 2 mol % SBA-15-TEMPO, 8 mol % FeCl<sub>3</sub>·6H<sub>2</sub>O, 10 mol % NaNO<sub>2</sub> in toluene under 1 atm O<sub>2</sub> at room temperature for 2 h, and the corresponding benzaldehyde product was obtained in 99.4% yield. Then we examined the efficiency of the catalyst SBA-15-TEMPO. When the loading of SBA-15-TEMPO was reduced from 2 mol % to 0.01 mol %, the product of benzaldehyde was still obtained in 97.7% yield. The TOF is up to 81.4 h<sup>-1</sup>, which is an excellent result for a room temperature aerobic alcohol oxidation involving a TEMPO catalyst. These results clearly illuminate that the supported TEMPO shows high activity for the oxidation of alcohol in the FeCl<sub>3</sub>·6H<sub>2</sub>O/TEMPO/NaNO<sub>2</sub> catalytic system.

Please cite this article in press as: Wang, L.; et al., Tetrahedron (2013), http://dx.doi.org/10.1016/j.tet.2013.05.076

Table 1        The result of the efficiency of the catalyst <sup>a</sup>									
OH SBA-15-TEMPO (x mol%), FeCl <sub>3</sub> 6H <sub>2</sub> O (8 mol%) NaNO <sub>2</sub> (10 mol%), toluene, 1 atm O <sub>2</sub> , 25 °C									
Entry	SBA-15-TEMPO (mol %)	<i>T</i> (h)	Yield <sup>b</sup> (%)	TOF $(h^{-1})$					
1	2	2	99.4	24.8					
2	0.5	4	96.3	48.1					
3	0.5	3	89.8	59.9					
4 <sup>c</sup>	0.01	120	97 7	814					

Benzyl alcohol 1 mmol.

b Determined by GC using internal standard method.

<sup>c</sup> TON: 9770.

The recyclability and the stability of the heterogeneous SBA-15-TEMPO catalyst are significant issues of our concern. There is an inevitable slight loss of the catalyst during the recovery steps. While considerable results could also be obtained using a lower loading of SBA-15-TEMPO, 2 mol % of SBA-15-TEMPO was used to examine the catalyst recyclability in order to reduce catalyst losses as much as possible. The reusability of the SBA-15-TEMPO catalyst was studied using benzyl alcohol as a model substrate. Since FeCl<sub>3</sub> cannot dissolve in toluene, the SBA-15-TEMPO and FeCl3 can be reused together. After fresh reaction, the reaction mixtures were washed with 3×5 mL toluene. Then, benzyl alcohol and NaNO<sub>2</sub> were added. The recycling results showed that the catalysts can be reused four times without significant loss of catalytic activity (Fig. 3). The fifth reaction can also give good result by prolonging



Fig. 3. Recyclability of the SBA-15-TEMPO+FeCl3·6H2O in the oxidation of benzyl alcohol.

the reaction time. The recyclability of the only SBA-15-TEMPO was also studied. After fresh reaction, the catalyst was filtrated off and washed with  $3 \times 5$  mL CH<sub>2</sub>Cl<sub>2</sub>, 5 mL water and  $3 \times 5$  mL acetone. The recovered catalyst was dried in air. The recycling results were shown in Fig.4. The catalyst SBA-15-TEMPO can be reused 10 times with a slight decrease in activity. This also suggests that the SBA-15-TEMPO catalyst shows high stability for the room temperature aerobic alcohol oxidation. An important feature is that the selectivity of the product is not affected during the recycling process.

To examine the practicability of the SBA-15-TEMPO catalyst for the alcohol oxidation, various alcohols including secondary aliphatic alcohols, benzylic alcohols, heterocyclic alcohols and also primary alcohols were oxidized to the corresponding carbonyl compounds in good to excellent yields and the results were summarized in Table 2. It is clear that the heterogeneous TEMPO catalyst shows excellent activity for the oxidation of alcohols at a low catalytic amount of SBA-15-TEMPO (0.1-1 mol %). Benzylic alcohols



Fig. 4. Recyclability of the SBA-15-TEMPO in the oxidation of benzyl alcohol.

#### Table 2

ОН

Oxidation of alcohols catalyzed by FeCl3·6H2O/SBA-15-TEMPO/NaNO2 under dioxygen atmosphere<sup>a</sup> SBA-15-TEMPO (x mol%), FeCl<sub>3</sub>·6H<sub>2</sub>O (8 mol%)

$R^1 \xrightarrow{\ \ R^2} R^2 \xrightarrow{\ \ NaNO_2 (10 \text{ mol}\%), \text{ toluene, } 1 \text{ atm } O_2, 25 ^{\circ}C} R^1 \xrightarrow{\ \ R^2}$						
Entry	$\mathbb{R}^1$	R <sup>2</sup>	SBA-15-TEMPO (mol %)	$T(\mathbf{h})$	Yield <sup>b</sup> (%)	
1	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	Me	1	12	>99	
2	$CH_3(CH_2)_2$	Me	1	12	97.3	
3	$(CH_3)_2CH_2$	Me	1	12	97.9	
4	Он	<o< td=""><td>1</td><td>20</td><td>50.9</td></o<>	1	20	50.9	
5	C <sub>6</sub> H <sub>5</sub>	Н	0.1	23	95	
6	p-Me-C <sub>6</sub> H <sub>4</sub>	Н	0.2	14	98.4	
7	p-Cl-C <sub>6</sub> H <sub>4</sub>	Н	0.5	12	>99	
8	p-Br-C <sub>6</sub> H <sub>4</sub>	Н	0.3	12	92.8	
9	p-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	Н	0.5	16	92.9	
10	$m-NO_2-C_6H_4$	Н	0.5	16	93.9 (93)	
11	0-NO2-C6H4	Н	1	14	97.0 (95)	
12	C <sub>6</sub> H <sub>5</sub>	Me	0.3	12	97.6	
13	m-Cl-C6H4	Me	0.5	12	93.4 (93)	
14	o-Cl-C <sub>6</sub> H <sub>4</sub>	Me	0.5	26	90.7	
15 <sup>c</sup>	m-Pyridyl	Н	1	12	61.3	
16 <sup>d</sup>	m-Pyridyl	Н	1	7	95.3	
17 <sup>d</sup>	o-Pyridyl	Н	1	6	92.8	
18	$CH_3(CH_2)_6$	Н	1	24	72.0	

<sup>1</sup> Alcohols 1 mmol.

<sup>b</sup> Determined by GC; values parenthesis are the yields of the isolated products.

<sup>c</sup> Reaction performed at 40 °C, 0.1 mL AcOH.

<sup>d</sup> Reaction performed at 60 °C. 0.1 mL AcOH.

containing electron-donating and electron-withdrawing groups proceeded readily to afford the desired products in excellent yields. The positions of the substituent on the benzene ring have a certain effect on the reactivity of benzylic alcohols. The substituent on the o-position of the benzene ring shows poorer activity than that of the *m*- and *p*-position. A larger amount of SBA-15-TEMPO and longer reaction time were required for the oxidation of osubstituted benzylic alcohols. The slow reaction rate of osubstituted benzylic alcohols can be ascribed to steric hindrance. Most of transition-metal-based catalytic systems are not capable of oxidizing the alcohols that contain heteroatoms, because of their strong coordination to metal centers. This catalytic system showed good tolerance for the heterocyclic substrates and gave good yields at an elevated temperature.

Using air instead of pure oxygen as oxidant has the obvious advantage of safety and low cost. We next examined the ability of the SBA-15-TEMPO catalyst to catalyze the alcohol oxidation using air instead of pure oxygen as terminal oxidant (Table 3). All alcohols

3

0

Please cite this article in press as: Wang, L; et al., Tetrahedron (2013), http://dx.doi.org/10.1016/j.tet.2013.05.076

#### 4

0

L. Wang et al. / Tetrahedron xxx (2013) 1–5

#### Table 3

Oxidation of alcohols catalyzed by  $\text{FeCl}_3\cdot\text{6H}_2\text{O}/\text{SBA-15-TEMPO}/\text{NaNO}_2$  under air atmosphere^a

$R^{1} \xrightarrow{\text{SBA-15-1EMPO}(0.5 \text{ mol}\%), \text{ FeCI}_{3}6H_{2}O(8 \text{ mol}\%)}_{\text{NaNO}_{2}(10 \text{ mol}\%), \text{ toluene, 1 atm air, 25 °C}} R^{1} \xrightarrow{\mathbb{R}^{2}}_{\text{R}^{2}}$							
Entry	R <sup>1</sup>	R <sup>2</sup>	<i>T</i> (h)	Yield <sup>b</sup> (%)			
1	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	Me	24	81.5			
2	$(CH_3)_2CH_2$	Me	24	74.4			
3	C <sub>6</sub> H <sub>5</sub>	Н	7	96.6 (91)			
4	p-Me-C <sub>6</sub> H <sub>4</sub>	Н	6	96.6 (94)			
5	p-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	Н	12	96.8			
6	$p$ -Br $-C_6H_4$	Н	12	>99			
7	C <sub>6</sub> H <sub>5</sub>	Me	6	98.5			
8	$m-Cl-C_6H_4$	Me	12	86.4			
9	o-Cl-C <sub>6</sub> H <sub>4</sub>	Me	28	94.1			

<sup>a</sup> Alcohols 1 mmol.

<sup>b</sup> Determined by GC; values parenthesis are the yields of the isolated products.

employed were oxidized to the corresponding aldehydes and ketones in good to excellent yields by prolonging the reaction time.

Finally, the gram-scale application of this catalytic system is also demonstrated and benzyl alcohol was taken as a test substrate (Scheme 1). A 50 mmol (5.4 g) reaction of benzyl alcohol was reacted with 0.2 mol % of SBA-15-TEMPO, 5 mol % FeCl<sub>3</sub>· $6H_2O$  and 5 mol % NaNO<sub>2</sub> in 20 mL toluene under oxygen atmosphere (balloon) at room temperature. The desired product was obtained in 94.5% yield within 34 h. The result suggests that the heterogeneous catalytic system is a highly practical application for aerobic alcohol oxidation in the laboratory.



Scheme 1. Large-scale benzyl alcohol oxidation.

# 3. Conclusions

In conclusion, an efficient room temperature oxidation of alcohols catalytic system using the mesoporous silica material SBA-15 functionalized TEMPO in combination with FeCl<sub>3</sub>·6H<sub>2</sub>O and NaNO<sub>2</sub> with oxygen or air as the environmentally benign oxidant has been developed. This heterogeneous catalytic system showed high activity for various alcohol oxidation to the corresponding carbonyl compounds in good to excellent yields with low catalytic amount of supported TEMPO (0.1-1 mol %), especially in the case of oxidation of secondary aliphatic alcohols to the corresponding ketones at room temperature. Based on a comparison with the known protocols for the commonly studied alcohols, this is the most efficient room temperature aerobic reaction with just 0.1-1 mol % of the TEMPO loading so far. Of particular importance, the catalyst could be recycled several times without significant loss of catalytic activity and the use of a low catalytic amount of SBA-15-TEMPO (0.2 mol %) on a large-scale experiment can afford the desired product in excellent yield. The distinctive feature of the catalysts is easy recovery and recycles, particularly the use of green and cheap iron salt and commercially available SBA-15, which makes the catalysts especially useful for practical applications.

# 4. Experimental section

# 4.1. General information

All chemical reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. All products were confirmed by GC–MS with Agilent 6890N GC/5973 MS detector and the comparison of their GC retention time with those of authentic samples. GC calculations of conversions and yields were performed on an Agilent 7890A with a flame ionization detector. SE-54 capillary column,  $30 \text{ m} \times 350 \text{ }\mu\text{m} \times 0.5 \text{ }\mu\text{m}$ ; FID detector, 300 °C; injection: 250 °C; carrier gas: nitrogen; carrier gas rate: 20 mL/min. All substrates and their corresponding products unless otherwise noted were detected under a condition: column temperature: 100 °C for 7 min, raising to 250 °C in a rate of 15 °C/min. 2-Pentanol and its corresponding product were detected under a condition: column temperature: 30 °C for 7 min, raising to 250 °C in a rate of 15 °C/min.

# 4.2. Synthesis of SBA-15

SBA-15 was synthesized according to the procedure from literature reported by Stucky and his co-workers.<sup>12</sup> In a typical preparation procedure, 4.0 g of Pluronic P123 copolymer surfactant  $(EO_{20}PO_{70}EO_{20} (C_3H_6O \cdot C_2H_4O)_x, M_w$ =5800 g/mol) was dissolved in 30 g of water, followed by addition of 120 g of 2 M HCl solution with stirring at 35 °C. After complete dissolution of P123 in the aqueous solution, 8.50 g of tetraethoxysilane (TEOS) was added with stirring at 35 °C for 20 h. Then, the mixture was transferred into an autoclave for condensation overnight at 80 °C. The solid obtained was filtered off and dried. The surfactant template was finally removed by extraction of the solid with ethanol containing HCl using a Soxhlet apparatus. SBA-15 was finally dried overnight at 110 °C under vacuum.

# 4.3. Synthesis of aminopropyl functionalized SBA-15 (SBA-15–NH<sub>2</sub>) $^{9\mathrm{a}}$

SBA-15–NH<sub>2</sub> was synthesized from the interaction between SBA-15 with APTES. In a typical preparation procedure, a suspension of freshly activated SBA-15 (5 g) with 3-aminopropyltriethoxysilane (APTES) (0.4 g) in dry toluene was refluxed overnight. The solid obtained was filtered off and washed with hot toluene using a Soxhlet apparatus. It was dried overnight at 110 °C under vacuum.

# 4.4. Synthesis of SBA-15-supported-TEMPO<sup>9a</sup>

A suspension of freshly activated SBA-15-NH<sub>2</sub> (1.5 g) in a dry CH<sub>3</sub>OH (8 mL), 4-oxo-TEMPO (0.75 mmol, 0.141 g) was added, followed by an excess of NaBH<sub>3</sub>CN (0.0625 g, 1 mmol). After stirring at room temperature for 3 days, the solid obtained was filtered off and thoroughly washed with hot methanol using a Soxhlet apparatus. It was dried overnight at 110 °C under vacuum.

# 4.5. Catalyst characterization

Small-angle X-ray powder diffraction was performed on a PANalytical X'PertPro-1 theta—theta system using Cu  $K\alpha$  radiation in continuous scan mode ranging from  $0.5^{\circ}-10^{\circ}$  operating at 40 mA and 40 kV. Data were analyzed using the PANalytical X'Pert High-Score Plus software package. N<sub>2</sub> sorption isotherms were measured at 77 K using a Quantachrome AUTOSORB-1 analyzer. Before the sorption measurements, samples were out gassed at 423 K for 6 h. Total pore volume was obtained from the volume of N<sub>2</sub> adsorbed at  $P/P_0=0.95$ . Pore diameter was calculated using the BJH model based on the adsorption branch of the isotherms. Specific surface areas were calculated using the BET model. Transmission electron micrographs (TEM) were acquired on a FEI Tecnai G2 Spirit at an acceleration voltage of 120 kV. The elemental analyses of catalysts

Please cite this article in press as: Wang, L.; et al., Tetrahedron (2013), http://dx.doi.org/10.1016/j.tet.2013.05.076

(C/H/N) were analyzed on a Perkin–Elmer 2400 CHN Elemental Analyzer.

## 4.6. Typical procedure for the oxidation of benzyl alcohol

A mixture of FeCl<sub>3</sub>·6H<sub>2</sub>O (8 mol %, 21.6 mg), SBA-15-TEMPO (2 mol %, 95.2 mg) in toluene (2 mL) was stirred for 1 min at room temperature in a 25 mL flask. Benzyl alcohol (1 mmol, 108 mg) was then added to the mixture. After stirring for 2 min, NaNO<sub>2</sub> (10 mol %, 6.9 mg) was added to the mixture. The resulting mixture was transferred to an autoclave. After the autoclave was closed, dioxygen was charged to 0.1 MPa. The progress of the reaction was monitored by GC using *n*-nonane as an internal standard.

# 4.7. General procedure for obtained isolated yield

After completion of the reaction, the reaction mixture was filtered off and washed with dichloromethane. The solvent was concentrated in vacuo and the product was further purified by column chromatography over silica gel with a mixture of ethyl acetate/hexane as eluent. <sup>1</sup>H and <sup>13</sup>C NMR spectra data of all isolated products were in accord with the literature.

### 4.8. The recovery of the SBA-15-TEMPO catalyst

After completion of the reaction, the reaction mixture was filtered off and catalyst was washed with  $3 \times 5$  mL CH<sub>2</sub>Cl<sub>2</sub>, 5 mL water and  $3 \times 5$  mL acetone. Then the recovered catalyst was dried in air.

## **References and notes**

- (a) Hudlicky, M. Oxidations in Organic Chemistry; American Chemical Society: Washington DC, 1990; (b) Larock, R. C. Comprehensive Organic Transformations; Wiley: New York, 1999; (c) Tojo, G.; Fernandez, M. Oxidations of Alcohols to Aldehydes and Ketones; Springer: New York, NY, 2006.
- March, J. Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, 4th ed.; John Wiley: New York, NY, 1992.
- For reviews of alcohol oxidation, see: (a) Mallat, T.; Baiker, A. Chem. Rev. 2004, 104, 3037; (b) Muzart, J. Tetrahedron 2003, 59, 5789; (c) Schultz, M. J.; Sigman, M. S. Tetrahedron 2006, 62, 8227; (d) Parmeggiani, C.; Cardona, F. Green Chem. 2012, 14, 547.
- For representative examples of transition-metal assisted TEMPO-catalyzed aerobic alcohols oxidations, see: (a) Semmelhack, F. M.; Schmidt, C. R.; Cortés, D. A.; Chou, C. S. J. Am. Chem. Soc. **1984**, 106, 3374; (b) Dijksman, A.; Marino-Gonzalez, A.; Mairata i Payeras, A.; Arends, I. W. C. E.; Sheldon, R. A. J. Am. Chem. Soc. **2001**, 123, 6826; (c) Ansariand, I. A.; Gree, R. Org. Lett. **2002**, 4, 1507; (d) Gamez, P.; Arends, I. W. C. E.; Reedijk, J.; Sheldon, R. A. Chem. Commun. **2003**, 2414; (e) Jiang, N.; Ragauskas, A. J. Org. Lett. **2005**, 7, 3689; (f) Wang, N. W.; Liu, R. H.; Chen, J. P.; Liang, X. M. Chem. Commun. **2005**, 5322; (g) Jiang, N.;

Ragauskas, A. J. J. Org. Chem. **2006**, 71, 7087; (h) Yin, W. L.; Chu, C. H.; Lu, Q. Q.; Tao, J. W.; Liang, X. M.; Liu, R. H. Adv. Synth. Catal. **2010**, 352, 113; (i) Jessica, M. H.; Stahl, S. S. J. Am. Chem. Soc. **2011**, 133, 16901 For representative examples of metal-free assisted TEMPO-catalyzed aerobic alcohols oxidations, see: (j) Liu, R. H.; Liang, X. M.; Dong, C. Y.; Hu, X. Q. J. Am. Chem. Soc. **2004**, 126, 4112; (k) Liu, R. H.; Dong, C. Y.; Liang, X. M.; Hu, X. Q. J. Org. Chem. Soc. **2004**, 126, 4112; (k) Liu, R. H.; Dong, C. Y.; Liang, X. M.; Hu, X. Q. J. Org. Chem. **2005**, 70, 729; (l) Xie, Y.; Mo, W. M.; Xu, D.; Shen, Z. L.; Sun, N.; Hu, B. X.; Hu, X. Q. J. Org. Chem. **2007**, 72, 4188; (m) Wang, X. L.; Liu, R. H.; Jin, Y.; Liang, X. M. Chem.—Eur. J. **2008**, 14, 2679; (n) He, X. J.; Shen, Z. L.; No, W. M.; Sun, N.; Hu, B. X.; Hu, X. Q. Adv. Synth. Catal. **2009**, 351, 829; (o) Miao, C. X.; He, L. N.; Wang, J. L.; Wu, F. J. Org. Chem. **2010**, 75, 257; (q) Wertz, S.; Studer, A. Adv. Synth. Catal. **2011**, 353, 69; (r) Wang, L. Y.; Li, J.; Lv, Y.; Zhao, G. D.; Gao, S. Appl. Organomet. Chem. **2012**, 26, 37 For reviews of TEMPO-catalyzed alcohol oxidation, see: (s) de Nooy, A. E. J.; Besemer, A. C.; van Bekkum, H. Synthesis **1996**, 1153; (t) Adam, W.; Saha-Moller, C. R.; Ganeshpure, P. A. Chem. Rev. **2001**, 101, 3499; (u) Sheldon, R. A.; Arends, I. W. C. E.; Brink, G.-J.; Dijksman, A. Acc. Chem. Res. **2002**, 35, 774.

- 5. Lu, Z. L.; Lindner, E.; Mayer, H. A. Chem. Rev. 2002, 102, 3543.
- (a) Dijksman, A.; Arends, I. W. C. E.; Sheldon, R. A. *Chem. Commun.* 2000, 271;
  (b) Dijksman, A.; Arends, I. W. C. E.; Sheldon, R. A. *Synlett* 2001, 102; (c) Tanyeli, C.; Gümüs, A. *Tetrahedron Lett.* 2003, 44, 1639; (d) Pozzi, G.; Cavazzini, M.; Quici, S.; Benaglia, M.; Dell'Anna, G. Org. Lett. 2004, 6, 441; (e) Ferreira, P.; Hayes, W.; Philips, E.; Rippon, D.; Tsang, S. C. *Green Chem.* 2004, 6, 310; (f) Ferreira, P.; Philips, E.; Rippon, D.; Tsang, S. C.; Hayes, W. J. Org. Chem. 2004, 69, 6851; (g) Gilhespy, M.; Lok, M.; Baucherel, X. *Chem. Commun.* 2005, 1085; (h) Anderson, C. D.; Shea, K. J.; Rychnovsky, S. D. Org. Lett. 2005, 7, 4879; (i) Wu, X. E.; Ma, L.; Ding, M. X.; Gao, L. X. *Synlett* 2005, 607; (j) Benaglia, M.; Puglisi, A.; Holczknecht, Q.; Quici, S.; Pozzi, G. *Tetrahedron* 2005, 348, 1016.
- 7. (a) Bolm, C.; Fey, T. Chem. Commun. 1999, 1795; (b) Ciriminna, R.; Bolm, C.; Avnir, D.; Pagliaro, M. Chem. Commun. 2000, 1441; (c) Fey, T.; Fischer, H.; Bachmann, S.; Albert, K.; Bolm, C. J. Org. Chem. 2001, 66, 8154; (d) Brunel, D.; Fajula, F.; Nagy, J. B.; Deroide, B.; Verhoef, M. J.; Veum, L.; Peters, J. A.; van Bekkum, H. Appl. Catal. A: Gen. 2001, 213, 73; (e) Ciriminna, R.; Bolm, C.; Fey, T.; Pagliaro, M. Adv. Synth. Catal. 2002, 344, 159.
- (a) Anelli, P. L.; Biffi, C.; Montanari, F.; Quici, S. J. Org. Chem. **1987**, 52, 2559; (b) Cecchetto, A.; Fontana, F.; Minisci, F.; Recupero, F. Tetrahedron Lett. **2001**, 42, 6651; (c) Minisci, F.; Recupero, F.; Cecchetto, A.; Gambarotti, C.; Punta, C.; Faletti, R.; Paganelli, R.; Pedulli, G. F. Eur. J. Org. Chem. **2004**, 109.
- (a) Karimi, B.; Biglari, A.; Clark, J. H.; Budarin, V. Angew. Chem., Int. Ed. 2007, 46, 7210; (b) Karimi, B.; Badreh, E. Org. Biomol. Chem. 2011, 9, 4194.
- (a) Corma, A. Chem. Rev. **1997**, 97, 237; (b) Wang, X.; Chen, C. C.; Chen, S. Y.; Mou, Y.; Cheng, S. Appl. Catal., A **2005**, 281, 47; (c) Martins, L.; Hölderich, W.; Hammer, P.; Cardoso, D. J. Catal. **2010**, 271, 220; (d) Rác, B.; Molnár, Á.; Forgo, P.; Mohai, M.; Bertóli, I. J. Mol. Catal. A: Chem. **2006**, 244, 46.
- (a) Newalker, B. L.; Clanrewaju, J.; Komarneni, S. Chem. Mater. 2001, 13, 552; (b) Newalkar, B. L.; Olanrewaju, J.; Komarneni, S. J. Phys. Chem. B 2001, 105, 8356; (c) Wu, P.; Tatsumi, T.; Komatsu, K.; Yashima, T. Chem. Mater. 2002, 14, 1657; (d) Ngamcharussrivichai, C.; Wu, P.; Tatsuimi, T. J. Catal. 2004, 227, 448; (e) Chen, S. Y.; Jang, L. Y.; Cheng, S. Chem. Mater. 2004, 16, 4174; (f) Vinu, A.; Sawant, D. P.; Ariga, K.; Hossain, K. Z.; Halligudi, S. B.; Hartmann, M.; Nomura, M. Chem. Mater. 2005, 17, 5339; (g) Chiang, C. W.; Wang, A.; Wan, B. Z.; Mou, C. Y. J. Phys. Chem. B 2005, 109, 18042; (h) Song, H.; Rioux, R. M.; Hoefelmeyer, J. D.; Komor, R.; Niesz, K.; Grss, M.; Yang, P.; Somorjai, G. A. J. Am. Chem. Soc. 2006, 128, 3027; (i) Chen, S. Y.; Tsai, H. D.; Chuang, W. T.; Lee, J. J.; Tang, C. T.; Lin, C. Y.; Cheng, S. J. Phys. Chem. C 2009, 113, 15226.
- (a) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, 279, 548; (b) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.