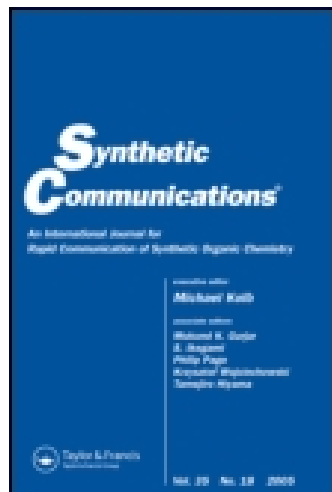


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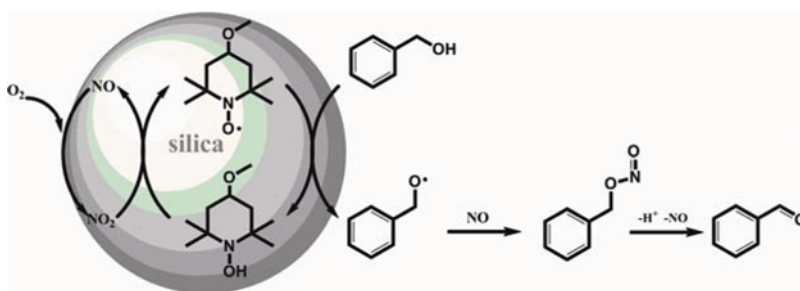
## SILICA-SUPPORTED 4-OH-TEMPO/NO<sub>x</sub>: A NOVEL AND EFFICIENT CATALYST FOR AEROBIC OXIDATION OF ALCOHOLS

Hua Zhang<sup>1</sup> and Luoling Fu<sup>2</sup>

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### GRAPHICAL ABSTRACT



**Abstract** Silica-supported 4-OH-2,2,6,6-tetramethylpiperidyl-1-oxy/NO<sub>x</sub> (4-OH-TEMPO) was immobilized on the surface of silica using the sol-gel method, and then it adsorbed NO<sub>x</sub>, as a heterogeneous catalyst, has exhibited good catalytic performance in alcohol oxidation. A broad range of alcohols were oxidized to their corresponding aldehydes or ketones with more than 99% selectivity and 99% conversion rate by such a catalyst system at room temperature in air. NO<sub>x</sub> not only acted as an electron bridge between O<sub>2</sub> and 4-OH-TEMPO but also were conducive to the formation of the aldehydes as active component. A possible mechanism for oxidation of alcohols promoted by silica-supported 4-OH-TEMPO/NO<sub>x</sub> was supposed.

[Supplementary materials are available for this article. Go to the publisher's online edition of Synthetic Communications<sup>®</sup> for the following free supplemental resource(s): Full experimental and spectral details.]

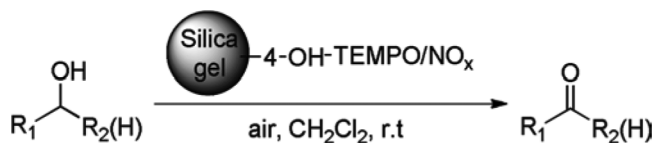
**Keywords** Alcohol oxidation; molecular oxygen; NO<sub>x</sub>; sol-gel; TEMPO

## INTRODUCTION

The selective oxidation of alcohols to the corresponding carbonyl compound is a fundamental transformation in organic synthesis reactions.<sup>[1–3]</sup> Traditionally, numerous stoichiometric amounts of chromium and manganese reagents<sup>[4]</sup> have been

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**Scheme 1.** Alcohol oxidation with silica-supported 4-OH-TEMPO/NO<sub>x</sub> system.

employed to accomplish this transformation. However, along with these processes, considerable problems, such as use of expensive reagents and serious effluent disposal problem, appear. To resolve these problems, molecular oxygen as the terminal oxidant for alcohol oxidation has attracted much attention in recent years.<sup>[5-7]</sup> Many highly efficient catalysts for the aerobic oxidation of alcohols using transition metals (such as copper salts, palladium, and ruthenium complexes)<sup>[8-12]</sup> have been developed recently. Furthermore, catalytic systems consisting of 2,2,6,6-tetramethylpiperidyl-1-oxy (TEMPO) for the selective aerobic oxidation of alcohols under mild conditions proved more efficient.

In the past two decades, many impressive in the combinations of diversified cocatalysts<sup>[13]</sup> with TEMPO in alcohol oxidation have been reported. The cocatalysts can be divided into two groups: transition-metal compounds [Fe(NO<sub>3</sub>)<sub>3</sub>, FeCl<sub>3</sub>, Cu (I) salts, Cu (II) salts, Ru complexes, etc.] and non-transition-metal compounds (NaNO<sub>2</sub>, *t*-BuONO, *m*-CPBA).<sup>[14,15]</sup> These catalysts have several advantages, such as good selectivity. However, they still suffer from drawbacks, such as multistep synthesis, tedious workup procedure for the recovery of the final products, due to homogeneous complex catalysts, and generation of copious amounts of toxic heavy-metal or halogen waste. Compared to homogeneous catalysts, heterogeneous catalysts have inherent advantages: easy separation and easy handling properties. There were also some reports on immobilized TEMPO (TEMPO immobilized on MCM-41, SBA-15, etc.), which combined with electron transfer compounds [such as *tert*-butyl nitrite (TBN), 1,3-dibromo-5,5-dimethylhydantoin (DBDMH), etc.] and exhibited good performance in selective oxidation of alcohols.<sup>[16-24]</sup> Hence, in view of atom economy, development of an efficient and selective heterogeneous catalyst that could utilize molecular oxygen as oxidant in alcohol translation under mild conditions is highly desirable.

Our previous work reported on the PSB-TEMPO-NO<sub>x</sub> system,<sup>[25]</sup> and we herein focus on developing catalysis system (silica-supported 4-OH-TEMPO/NO<sub>x</sub>), in which 4-OH-TEMPO was immobilized on the surface of silica by using the sol-gel method and then absorbing molecular nitrogen oxide (NO<sub>x</sub>), with activated molecular oxygen as oxidant in alcohol oxidation. In the presence of silica supported 4-OH-TEMPO/NO<sub>x</sub>, many benzylic alcohols and secondary alcohols can be oxidized to their corresponding aldehydes or ketones in 7 h with more than 99% conversion and about 99% selectivity just at room temperature in an air atmosphere (Scheme 1).

## RESULTS AND DISCUSSION

### Characterization of Catalyst

The degree of functionalization of silica-supported 4-OH-TEMPO was calculated on the basis of the nitrogen content in the catalyst (Table 1, entry 1), the final

**Table 1.** Elemental analysis results of catalysts

Entry	Catalyst	C (%) <sup>a</sup>	H (%) <sup>a</sup>	N (%) <sup>a</sup>	Cat (mmol · g <sup>-1</sup> )	NO <sub>x</sub> (mmol · g <sup>-1</sup> )
1	Silica-supported 4-OH-TEMPO	5.575	2.941	0.199	0.142	0
2	Silica-supported 4-OH-TEMPO/NO <sub>x</sub>	5.013	3.010	1.446	0.142	0.891
3	Silica-supported 4-OH-TEMPO/NO <sub>x</sub> (V) <sup>b</sup>	4.448	2.546	0.509	0.142	0.221

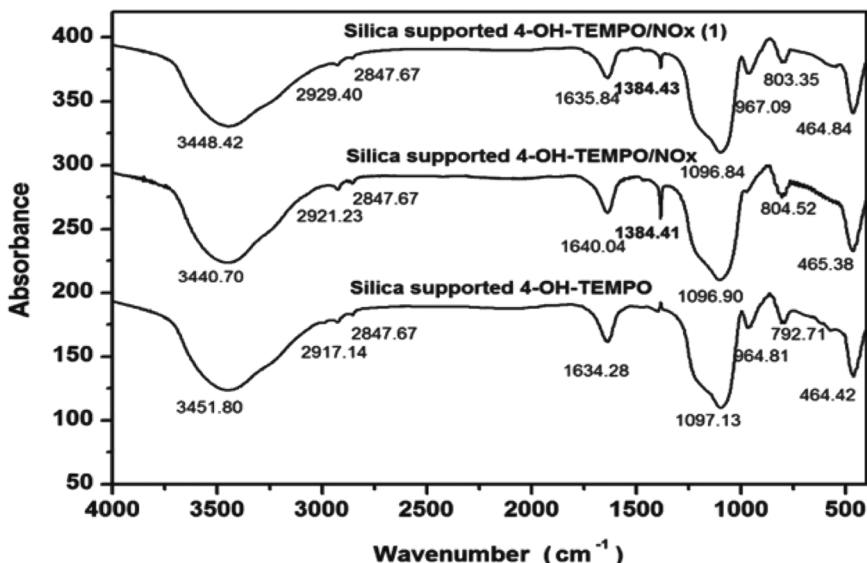
<sup>a</sup>Quality percentage.

<sup>b</sup>Silica-supported 4-OH-TEMPO/NO<sub>x</sub> had been used five times.

value was 0.142 mmol · g<sup>-1</sup>. Through comparing nitrogen content of silica-supported 4-OH-TEMPO/NO<sub>x</sub> with nitrogen content of silica-supported 4-OH-TEMPO, the amount of the absorbed NO<sub>x</sub> was detected, and the value was 0.891 mmol · g<sup>-1</sup>. The values indicated that the sol-gel immobilization method could give a good degree of functionalization and also absorb NO<sub>x</sub> well. Moreover, the immobilization of TEMPO by the sol-gel technique saves more time and was cleaner than other immobilization method in benzene or toluene. Even when reused five times, there was still 0.221 mmol · g<sup>-1</sup> NO<sub>x</sub> left in the catalyst.

In the IR spectra (Fig. 1), a new absorption peak near 1384.41 cm<sup>-1</sup> appeared, which suggested that NO<sub>x</sub> successfully was stored in catalysts by this preparation method because such peak is corresponding to the vibration of NO<sub>3</sub><sup>+</sup>.<sup>[26]</sup> In the infrared (IR) spectrum of silica-supported 4-OH-TEMPO/NO<sub>x</sub>(1), the intensity of a peak near 1384.41 cm<sup>-1</sup> decreased obviously but still can be found, which indicated that NO<sub>x</sub> still existed in catalyst after being used once.

The specific surface area, pore volumes, and pore diameter of samples are presented in Table 2. After the silica-supported 4-OH-TEMPO/NO<sub>x</sub> have been used,



**Figure 1.** FT-IR spectra of catalysts (silica-TEMPO/NO<sub>x</sub>(1) has been used once).

**Table 2.** Physical data of catalysts

Physical data	Silica-supported 4-OH-TEMPO	Silica-supported 4-OH-TEMPO/NO <sub>x</sub> (1) <sup>c</sup>	Silica-supported 4-OH-TEMPO/NO <sub>x</sub> (V) <sup>d</sup>
BET surface area [m <sup>2</sup> ·g <sup>-1</sup> ]	559.5716	622.2915	845.7917
Pore volume <sup>a</sup> [cm <sup>3</sup> ·g <sup>-1</sup> ]	0.131232	0.145596	0.245962
Average pore diameter <sup>b</sup> [nm]	2.5045	2.5229	2.6765

<sup>a</sup>Diameters of the pores are between 1.7000 and 300.0000 nm.

<sup>b</sup>BJH adsorption average pore diameter (4V/A).

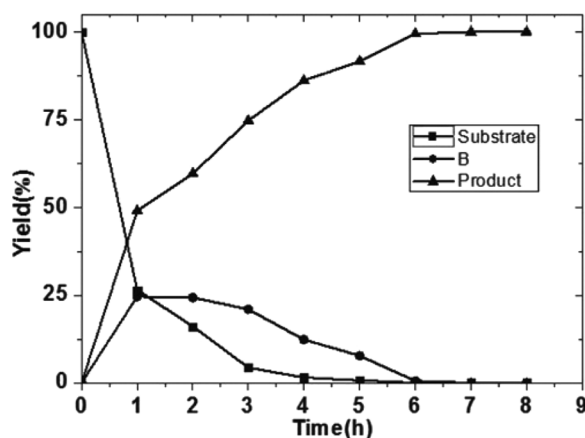
<sup>c</sup>Silica supported 4-OH-TEMPO has been used once.

<sup>d</sup>Catalyst has been used five times.

the BET surface area and pore volume of samples gave an apparent increase, which clearly suggested that the catalyst particles were broken into small sizes, which means that the catalyst cannot be reused more times. The average pore diameter between the three samples did not change obviously, indicating that a very acute scarcity of 4-OH-TEMPO dropped from silica and suggesting that the catalyst physical characters were not affected after oxidation reaction.

### Aerobic Oxidation of Alcohols

A typical time course for the silica-supported 4-OH-TEMPO/NO<sub>x</sub>-catalyzed oxidation of benzyl alcohol under optimized conditions is shown in Fig. 2. The starting substrate was completely oxidized into benzaldehyde within 7 h. It is worth mentioning that no benzoic acid was detectable throughout the oxidation process. However, during the reaction, there was an intermediate product B (benzyl nitrite<sup>[27]</sup>). When the catalyst was added into the reaction solution, benzyl nitrite can be detected. As reaction time increased, the content of benzyl nitrite increased gradually, and the maximum value could be up to 25%. Then the value decreased



**Figure 2.** Representative time course of silica-supported 4-OH-TEMPO/NO<sub>x</sub> catalyzed oxidation. Benzyl alcohol to benzaldehyde, B is intermediate product benzyl nitrite.

with time until finally benzyl nitrite could not be detected. Meanwhile, the product consistently increased from 0 to 100% until completion of the oxidation. The mass spectrum (MS) of benzyl nitrite was collected by analyzing the 1 h reaction mixture on gas chromatography–mass spectrometry (GC-MS).

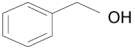
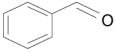
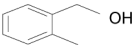
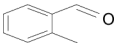
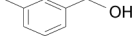
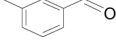
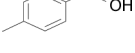
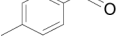
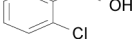
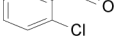
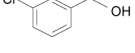
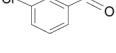
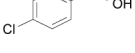
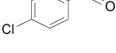
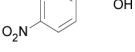
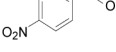
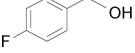
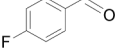
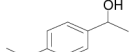
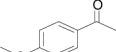
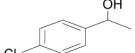
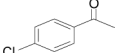
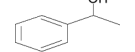
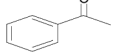
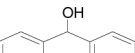
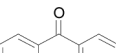
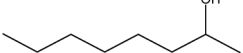
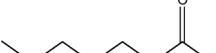

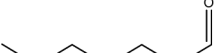
Table 3 shows that various types of benzylic alcohols were readily oxidized with complete conversion and good selectivity to their corresponding aldehydes by this catalytic system (entries 1–7). However, electron-rich and electron-deficient substrates showed a little difference (entries 9 and 10), where more hours to oxidize were needed than the others. It is worth mentioning that the system also showed good activity in oxidizing different types of secondary alcohols to their corresponding ketones (entries 10–13) without any side products. The only shortcoming is that secondary alcohol oxidation needs more time than primary alcohols. Silica-supported 4-OH-TEMPO/NO<sub>x</sub> (as an example of immobilized 4-OH-TEMPO combining with NO<sub>x</sub>), a heterogeneous catalysis system, activated molecular oxygen for selective alcohol oxidation successfully. Translating aliphatic alcohol into their corresponding products (entries 14 and 15) proved more challenging for this system.

In addition, reusability of the catalyst was confirmed in five recycling experiments. At the end of each run, the catalyst was separated by filtration, extracted with Soxhlet with dichloromethane, and dried in air for 3 h, and then NO<sub>x</sub> was absorbed. The results in Fig. 3 revealed that the selectivity for benzaldehyde was unaffected. However, the conversion of benzyl alcohol oxidation decreased marginally from 100 to 95% after reusing silica-supported 4-OH-TEMPO/NO<sub>x</sub> five times. The elemental composition of catalyst (C and H) confirmed that this marginal decrease in catalytic activity was not due to leaching of TEMPO but breaking the catalyst under magnetic stirring, which resulted in the decrease of NO<sub>x</sub> and product molecule adsorption.

There were some reported mechanisms of alcohol oxidation; for examples, the mechanism of corresponding oxoammonium cation is the active oxidant in TEMPO/sodium hypochlorite or sodium bromide systems.<sup>[15]</sup> In our work, we found an interesting phenomenon during the process of catalyst preparation and alcohol oxidation (i.e., the color changes of catalysts). The transparent white silica turned light yellow after being grafted with TEMPO, and then it changed to orange when absorbing NO<sub>x</sub>. After the catalyst was added into alcohol methylene chloride solution, it turned light yellow again. However, as the reaction went on, the color of silica disappeared and then turned orange gradually. When the color of catalyst in the reaction mixture returned to the primary color, the oxidation process was finished.

Meanwhile, combining with the intermediate (benzyl nitrite) detected, a proposed (benzyl alcohol was taken as an example) oxidation mechanism (Scheme 2) is given. First, the immobilized TEMPO was oxidized to TEMPO<sup>+</sup> by adsorbed NO<sub>2</sub>; meanwhile, NO<sub>2</sub> was reduced to NO (NO would be reoxidized by O<sub>2</sub> diffusing into the pore canals from the air). Second, the alcohols diffusing into the pore canal of silica and got in touch with TEMPO<sup>+</sup> and NO<sub>x</sub>, and then they were oxidized by TEMPO<sup>+</sup>. The oxidized product reacted with NO, generating benzyl nitrite, and at the same time TEMPO<sup>+</sup> was reduced to TEMPOH, which entered the next cycle. Finally, benzyl nitrite diffused out of the pore canal and lost H<sup>+</sup> and NO, forming the carbonyl compound. When the oxidation process was completed, the silica pores were full of NO<sub>x</sub>, which present orange, so the catalyst showed orange. During the

**Table 3.** Aerobic oxidation of alcohols using silica-supported 4-OH-TEMPO/NO<sub>x</sub><sup>a</sup>

Entry	Substrate	Product	Con/Sel (%)	Time (h)
1			100/99	7
2			100/99	7
3			100/99	7
4			100/99	7
5			100/99	7
6			100/99	7
7			100/99	7
8			100/99	8
9			100/99	7
10			100/99	7
11			100/99	9
12			100/99	15
13			100/99	18
14			90/76	24
15			— <sup>b</sup>	24

<sup>a</sup>Substrate (1 mmol), silica-supported 4-OH-TEMPO/NO<sub>x</sub> (0.5 g), CH<sub>2</sub>Cl<sub>2</sub> (6 mL), room temperature, and ambient pressure. Conversion and selectivity determined by GC.

<sup>b</sup>No product was detected.



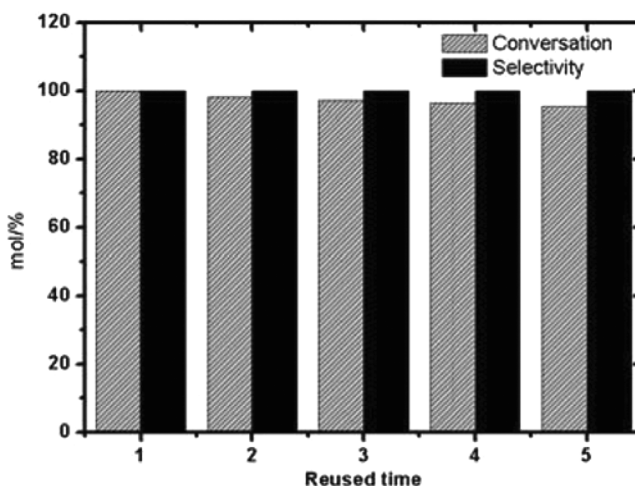
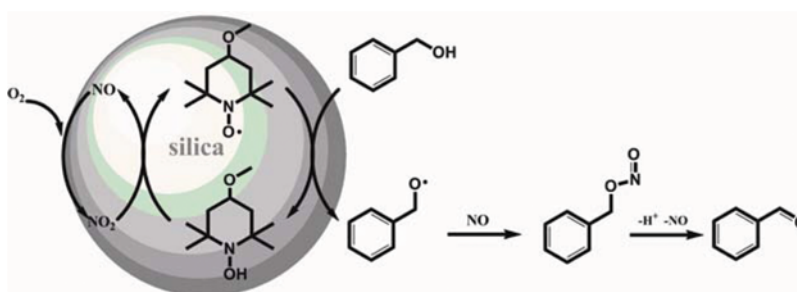


Figure 3. Reusability of silica-supported 4-OH-TEMPO/NO<sub>x</sub>.

entire process, NO<sub>x</sub> not only acts as an electron bridge between O<sub>2</sub> and TEMPO but also as conducive to the formation of the aldehyde as active compound. If the silica has enough mechanical strength and would not break into smaller pieces under magnetic stirring, NO<sub>x</sub> should remain stored in silica pores after reaction and thus the catalyst could be reused without a second NO<sub>x</sub> adsorption. This might be another promising bright spot for such a catalytic system.

In summary, we have reported a simple and time-saving sol-gel method to immobilize 4-OH-TEMPO on the silica surface. Silica-supported 4-OH-TEMPO/NO<sub>x</sub> is a good catalyst for the selective oxidation of alcohols. It enabled us to utilize O<sub>2</sub> as a clean terminal oxidant to promote alcohol oxidations at room temperature under a normal atmosphere. The catalyst also showed good recyclability just by filtering from the reaction mixture and reabsorbing NO<sub>x</sub>. Furthermore, the mechanism we proposed is particularly well suited for the alcohol oxidation by TEMPO combining with NO<sub>x</sub>. We believed that NO<sub>x</sub> combined with immobilized TEMPO for aerobic oxidation of alcohols will be widely used in the near future.



Scheme 2. Proposed mechanism. (Figure is provided in color online.)

## EXPERIMENTAL

### Materials and Methods

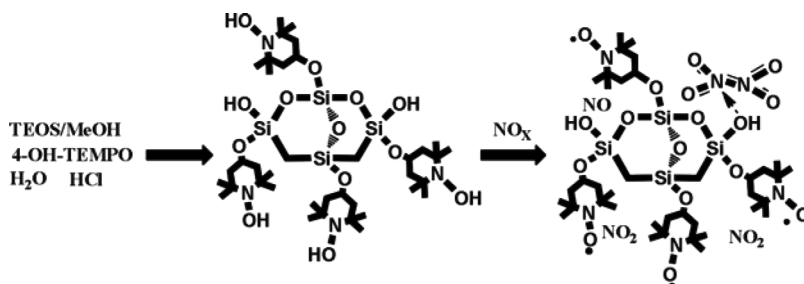
All the alcohols were purchased from Across, Alfa Aesar, and Energy chemical companies and were used without further purification. The intermediate products were identified by GC-MS (Agilent 5975). The final products were examined by  $^1\text{H}$  and  $^{13}\text{C}$  NMR analysis (Bruker spectrometer 400 MHz) in  $\text{CDCl}_3$  with tetramethylsilane (TMS) as internal standard. Conversions and selectivities were based on GC (Agilent 6890N) with area normalization method.

### Catalyst Preparation and Characterization

**Preparation of silica-supported 4-OH-TEMPO.** 4-OH-TEMPO (0.742 g), and was suspended in anhydrous methanol (25 mL), and then tetraethyl orthosilicate (33 mL) and hydrochloric acid (38% 0.5 mL) were added dropwise into the solution. The reaction mixture was stirred at room temperature for 2 h until a clear and homogeneous liquid mixture was formed. The mixture was aged for 12 h in air. The resulting solid material was dried at  $45^\circ\text{C}$  for 2 days, and then underwent soxhlet extraction with dichloromethane for 8 h. Thus 6.3 g of silica-supported 4-OH-TEMPO was obtained.

**$\text{NO}_x$  adsorption.** Sulfuric acid solution ( $\text{H}_2\text{SO}_4\text{-H}_2\text{O} = 1:2$  [v/v], 8 mL) was placed in a separatory funnel and dropped onto sodium nitrite (4.0 g), which was placed in a jar for 30 min. The  $\text{NO}_x$  gas that came into being was first dried by a calcium chloride tube, then fed into a adsorption tube (12 mm inside diameter and 8 cm length) in which the silica-supported 4-OH-TEMPO (0.5 g) was placed, and finally introduced into a tail gas adsorber. The overall adsorption time was 1 h. When the  $\text{NO}_x$  adsorption was finished, the connection between the calcium chloride tube and the adsorption tube was shut down, while keeping the connection between the adsorption tube and tail gas adsorber open for 0.5 h to release the physisorbed  $\text{NO}_x$  from the surface of silica supported 4-OH-TEMPO. In this way, we got silica-supported 4-OH-TEMPO/ $\text{NO}_x$  (Scheme 3).

**Characterization of catalysts.** Silica-supported 4-OH-TEMPO, silica-supported 4-OH-TEMPO/ $\text{NO}_x$ , and silica-supported 4-OH-TEMPO/ $\text{NO}_x(1)$  (silica-supported 4-OH-TEMPO/ $\text{NO}_x$  which had been used one time) were analyzed.



Scheme 3. Preparation of silica-supported 4-OH-TEMPO/ $\text{NO}_x$ .

Physical data of samples were measured using a Micromeritics ASAP 2020 physical adsorption apparatus. All materials were degassed for 4 h under 100 °C before being analyzed at 77 K to measure nitrogen adsorption/desorption isotherms. The specific surface area of sample was calculated using the BET (Brunauer–Emmett–Teller) equation. The Barrett–Joyner–Halen (BJH) model was used to obtain the adsorption branches of the isotherms, from which the pore diameters were derived. The pore volumes were determined according to the BJH adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter. Elemental-analyses (C, H, N on Elemental Vario EL III) and Fourier transform–infrared (FT-IR) spectroscopy were employed to study the immobilization of 4-OH-TEMPO.

### General Procedure for the Aerobic Oxidation

In a typical oxidation reaction, alcohol substrate (1 mmol), silica-supported 4-OH-TEMPO/NO<sub>x</sub> (0.5 g), and methylene dichloride (6 mL) were placed in a 50 mL long-necked, round-bottom flask equipped with a ground-glass elbow to get in touch with the atmosphere. The resulting mixture was magnetically stirred at room temperature and ambient pressure. The reaction was monitored by TLC and GC with a HP-5 capillary column and an FID detector. When the reaction completed, the catalyst was separated from the reaction mixture by vacuum filtration, during which the catalyst was washed five times with dichloromethane (10 mL), dried in air, and then adsorbed NO<sub>x</sub> gas for reuse. The filtrate was separated and solvent removed under reduced pressure. The final product was examined by <sup>1</sup>H and <sup>13</sup>C NMR analysis.

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### REFERENCES

1. Sheldon, R. A.; Arends, I. W. C. E.; Ten Brink, G. J.; Dijkman, A. *Acc. Chem. Res.* **2002**, *35*, 774–781.
2. Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981.
3. Vazyliev, M.; Sloboda-Rozner, D.; Haimov, A.; Maayan, G.; Neumann, R. *Topics Catal.* **2005**, *34*, 93.
4. March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 4th ed.; John Wiley & Sons: New York, 1992.
5. Noyori, R.; Aoki, M.; Sato, K. *Chem. Commun.* **2003**, 1977–1986.
6. Mallat, T.; Baiker, A. *Chem. Rev.* **2004**, *104*, 3037–3058.
7. Ten Brink, G. J.; Arends, I. W. C. E.; Sheldon, R. A. *Science*. **2000**, *287*, 1636–1639.
8. Lin, L.; Ji, L. Y.; Wei, Y. Y. *Catal. Commun.* **2008**, *9*, 1379–1382.
9. Figiel, P. J.; Leskela, M.; Repo, T. *Adv. Synth. Catal.* **2007**, *349*, 1173–1179.
10. Ten Brink, G. J.; Arends, I. W. C. E.; Sheldon, R. A. *Adv. Synth. Catal.* **2002**, *344*, 355–369.

11. Arends, I. W. C. E.; Ten Brink, G. J.; Sheldon, R. A. J. *Mol. Catal. A: Chem.* **2006**, *251*, 246–254.
12. Matsumoto, T.; Ueno, M.; Kobayashi, J.; Miyamura, H.; Mori, Y.; Kobayashi, S. *Adv. Synth. Catal.* **2007**, *349*, 531–534.
13. Vogler, T.; Studer, A. *Synthesis* **2008**, *13*, 1979–1993.
14. Wang, X. L.; Liang, X. M. *Chin. J. Catal.* **2008**, *29*, 935–939.
15. Wang, N. W.; Liu, R. H.; Chen, J. P.; Liang, X. M. *Chem. Commun.* **2005**, 5322–5324.
16. Gilhespy, M.; Lok, M.; Baucherel, X. *Chem. Commun.* **2005**, 1085–1086.
17. Chung, C. W. Y.; Toy, P. H. J. *Comb. Chem.* **2007**, *9*, 115–120.
18. Qu, J. Q.; Katsumata, T.; Satoh, M.; Wada, J.; Masuda, T. *Polymer* **2009**, *50*, 391–396.
19. Subhani, M. A.; Beigi, M.; Eilbracht, P. *Adv. Synth. Catal.* **2008**, *350*, 2903–2909.
20. Qian, W. X.; Jin, E. L.; Bao, W. L.; Zhang, Y. M. *Tetrahedron* **2006**, *62*, 556–562.
21. Bolm, C.; Fey, T. *Chem. Commun.* **1999**, 1795–1796.
22. Tsubokawa, N.; Kimoto, T.; Endo, T. J. *Mol. Catal. A: Chem.* **1995**, *101*, 45–50.
23. Fey, T.; Fischer, H.; Bachmann, S.; Albert, K.; Bolm, C. J. *Org. Chem.* **2001**, *66*, 8154–8159.
24. Karimi, B.; Biglari, A.; Clark, J. H.; Budarin, V. *Angew. Chem.* **2007**, *119*, 7348–7351.
25. Lei, D.; Zhang, H. *Adv. Synth. Catal.* **2011**, *353*, 1253–1259.
26. Al-Abadleh, H. A.; Grassian, V. H. *J. Phys. Chem. B* **2003**, *107*, 10829–10839.
27. Sheng, X. B.; Ma, H.; Chen, C.; Gao, J.; Yin, G. C.; Xu, J. *Catal. Commun.* **2010**, *11*, 1189–1192.