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Article

Silica gel-supported TEMPO with adsorbed NO_x for selective oxidation of alcohols under mild conditions

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A column padding silica gel was used to support 2,2,6,6-tetramethylpiperdine-1-oxyl (TEMPO) and to adsorb NO_x to provide an oxidant system for the selective oxidation of alcohols. A wide range of alcohols were oxidized to the corresponding aldehydes and ketones with high selectivities and conversions using this heterogeneous catalyst under mild conditions.

1. Introduction

As one of the most important oxidation reactions, the selective oxidation of alcohols to the corresponding carbonyl compounds is used in the synthesis of organic intermediates and fine chemicals [1,2]. Many efficient methods have been developed for the selective oxidation of alcohols using a variety of oxidizing agents and catalysts, including stoichiometric oxygen donors [3,4], metal catalysts, and N-oxide catalysts [5–10]. However, these methods for the oxidation of alcohols suffer from drawbacks such as the use of at least a stoichiometric amount of oxidant, giving a large quantity of harmful byproducts and requiring high temperature and high pressure conditions in the oxidation process. For decreasing environmental and economic stress, another approach to construct a clean catalytic system for the oxidation of alcohols, such as using molecular oxygen [11] (H_2O_2, O_2, O_3, etc.) as oxidant has become popular in recent years.

In the past two decades, N-oxides as valuable catalysts for the aerobic oxidation of various organic compounds under mild reaction conditions have become increasingly attractive [12]. 2,2,6,6-tetramethylpiperdine-1-oxyl (TEMPO), which can oxidize various kinds of alcohols into their corresponding aldehydes and ketones, is more stable and efficient [13] than other N-oxides. It has the advantages of high efficiency, high selectivity, and easy handling and is environmentally friendly for the oxidation of alcohols. TEMPO also expressed nearly quantitative oxidation [14–16] and has been applied in industry successfully [17]. In particular, TEMPO in combination with an active molecular oxygen co-catalyst as a catalytic system to oxidize alcohols has become attractive recently [18–21]. Following Anelli's TEMPO/NaBr/NaOCl system, a series of TEMPO in combination with active molecular oxygen co-catalysts as terminal oxidant systems such as TEMPO/NaBr/$NaNO_2$ [19], H_2O_2/HBr/$NaNO_2$ [20], and TEMPO/HBr/TBN [21] have been developed as efficient methods for the oxidation of alcohols. However, some of these systems use Br, which is not considered friendly to the environment, some need demanding condi-

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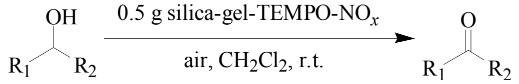


Scheme 1. Alcohol oxidation with the silica gel-TEMPO-NO$_x$ system in air.

tions, and some need multistep product separation. Efforts to develop a new oxidant system are required to overcome these inherent shortcomings. TEMPO immobilized on a mesoporous material [22,23] combined with an active molecular oxygen co-catalyst in the field of alcohol oxidation has become more attractive.

Silica gel consists of many pores and a large surface area, which provide sites for the immobilization of TEMPO and the storage of NO$_x$. Since it was reported recently that NO_2 oxidized TEMPO into the TEMPO cation to initiate alcohol oxidation and NO$_x$ was removed by silica-supported aminoxyls [24,25], we envision that NO$_x$ can be used as the direct electron bridge between TEMPO and molecular oxygen. Thus the use of silica gel-supported TEMPO with adsorbed NO$_x$ as a catalytic system for the oxidation of alcohols may be efficient. Our previous work reported the PSB-TEMPO-NO$_x$ system [26]. Here our interest was in designing NO$_x$ storage in padding silica gel-TEMPO material as a heterogeneous oxidation system for the selective oxidation of alcohols (Scheme 1) under mild conditions.

The supported TEMPO catalyst was obtained by direct grafting of silica gel with 3-(triethoxysilyl) propamino-TEMPO, which was prepared following the procedure described by Ciriminna et al. [27], as silylating agent [28] (Scheme 2). Functionalized and unfunctionalized silica gel were characterized by N_2 adsorption and Fourier transform infrared spectroscopy (FT-IR). The functional group contents of the surface were obtained from elemental analysis. The quantitative determination of NO$_x$ adsorbed content was measured by NO$_x$ temperature-programmed desorption (NO$_x$-TPD), which was also compared with the elemental analysis (C, H, N) values.

2. Experimental

2.1. Catalyst preparation

4-oxo-TEMPO was synthesized according to the literature [29]. 4-oxo-TEMPOH (0.704 g, 4 mmol), APTES (0.884 g, 4 mmol), and methanol (8.5 mL) were added into a 100 mL flask with vigorous stirring for 2 h. Then $NaBH_3CN$ (0.25 g, 6 mmol) was added, and the mixture was stirred at ambient temperature for 12 h. The pH was adjusted to 3–4 with HCl (38%), and 2 g of SPE column packing silica gel (Dalian Sipore Co. Ltd., the particle and pore size of the SPE padding silica were 40 μm diameter and 10 nm, respecitvely) was suspended in the mixture with gentle agitation. After 24 h reaction, the catalyst was filtered, washed in a Soxhlet apparatus with CH_2Cl_2 for 20 h, and then dried in a vacuum oven at 45 °C for 3 h. After evaporation of the solvent, 2.130 g of silica gel-supported TEMPO was obtained.

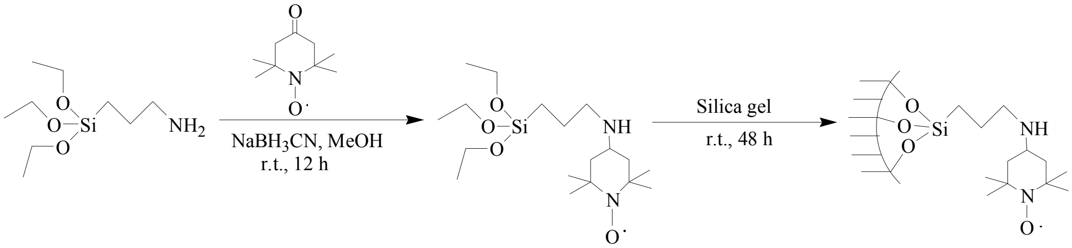
The NO$_x$ adsorption procedure was as follows. A 5 mL of H_2SO_4 solution (H_2SO_4:H_2O = 1:2, v:v) was placed in a separatory funnel, and 5 g of $NaNO_2$ was placed in a jar. The acid solution was dropped into the sodium nitrite over 30 min. After the silica gel–supported TEMPO (0.5 g) was placed in an adsorption tube (10 cm length and 15 mm inside diameter), NO$_x$ gas, which was first dried by a $CaCl_2$ tube, was fed into the adsorption tube and finally introduced into a tail gas absorption device. The adsorption was allowed to continue for 1 h. Then the connection was shut down between the calcium chloride tube and the adsorption tube. Meanwhile the connection between the $CaCl_2$ tube and tail gas absorption device was opened for 2 h to release physisorbed NO$_x$ from the surface of the silica gel-supported TEMPO. Finally, silica gel-supported TEMPO/NO$_x$ was obtained.

2.2. Catalyst characterization

All materials were degassed for 4 h at 100 °C before using a Micromeritics ASAP 2020 physical adsorption apparatus at −196 °C to measure the N_2 adsorption isotherms. The specific surface area of the samples was calculated by the BET equation. Pore volume was obtained by the BJH method for adsorption cumulative volume of pores between 1.7 and 300 nm diameter. The BJH model was used to derive the pore diameter distributions from the adsorption branch of the isotherm. NO$_x$ absorption was analyzed by elemental analysis on an Elemental Vario EL III and by FT-IR spectroscopy. NO$_x$-TPD was conducted by the method of putting the catalyst (0.05 g) in a homemade desorption tube with temperature-programmed heating of the tube from 25 to 500 °C in a 80 mL/min of N_2 flow at 20 °C/min. A chemiluminesence detector (Ecophysis CLD 60) was applied to analyze the outlet gas composition online.

2.3. Aerobic oxidation

All the alcohols were purchased from Acros, Alfa Aesar, and Energy Chemical Companies and used without further purification. A solution of alcohol substrate (1.0 mmol) in CH_2Cl_2 (6 mL) was prepared in a 50 mL long-necked, round-bottom flask



Scheme 2. Synthesis of silica gel-supported TEMPO.

Table 1
Elemental analysis of catalysts.

Catalyst	C[a] (%)	H[a] (%)	N[a] (%)	Catalyst (mmol/g)	NO_x (mmol/g)
Silica	0.055	2.341	0.010	0	0
Silica gel-TEMPO	5.430	2.670	0.819	0.292	0
Silica gel-TEMPO-NO_x	5.013	2.387	1.868	0.292	0.749
Silica gel-TEMPO-NO_x(1) [b]	5.077	2.057	1.292	0.292	0.337

[a] Quality percentage.
[b] Silica gel-TEMPO-NO_x that was used once.

equipped with a ground glass elbow to be in contact with the atmosphere. Then silica gel-supported TEMPO/NO_x (0.5 g) was added, and after that the resulting mixture was magnetically stirred at room temperature and ambient pressure. TLC and GC (GC Agilent 6890N) were applied to monitor the reaction. When the reaction was over, the mixture was vacuum filtered to get the product, which was examined by ^1H and ^{13}C NMR analysis (Bruker spectrometer, 400 MHz) with $CDCl_3$ as the solvent and TMS as internal standard. The area normalization method was applied to calculate conversion and selectivity of the oxidation from GC results.

3. Results and discussion

3.1. Synthesis of immobilized TEMPO

Silica gel-supported TEMPO was achieved by the direct functionalization of the silica gel surface with a silylating agent (Scheme 2), which was prepared with 4-oxo-TEMPO as the starting material. Our immobilization method involved just stirring in methanol and Saxhlet extraction with CH_2Cl_2. All the reagents were used without any further treatment. This method is green and time-saving and has the same positive effects as other immobilization methods that need treatment in dry toluene and dry methanol for several days.

3.2. Characterization of the materials

3.2.1. Elemental analysis and FT-IR study

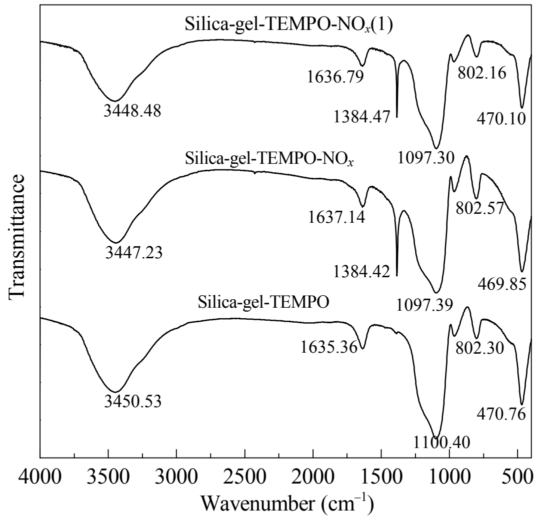


Fig. 1. FT-IR spectra of the silica gel-TEMPO sample.

The elemental analysis of catalysts is shown in Table 1. The degree of functionalization of silica gel-TEMPO was calculated on the basis of the increase of nitrogen content in comparison to that of the non-modified support. The final value was 0.292 mmol/g. As shown in Table 1, the amount of absorbed NO_x was 0.794 mmol/g, and even after one usage, there was 0.337 mmol/g NO_x left. This indicates that this immobilization method gave a good degree of functionalization and the prepared material also adsorbed NO_x well.

FT-IR spectrum changes were observed for the samples of silica gel-TEMPO-NO_x and silica gel-TEMPO. It was reported that NO_2 oxidized TEMPO into $TEMPO^+$, and NO_2 changed to NO_3^-, which has been studied with the V3(NO_3^-) band seen near 1388 cm^{-1} [30]. Our system also contained these reactions. The sharp peak at 1384 cm^{-1} corresponds to NO_x adsorbed by silica gel-TEMPO-NO_x and silica gel-TEMPO-NO_x (1) (Fig. 1). Obviously, the FT-IR spectra showed that the NO_x storage was successful in the preparation. In addition, the 1384 cm^{-1} peak over silica gel-TEMPO-NO_x(1) spectrum also gave clear evidence that there was still NO_x left in the catalyst after it was used once.

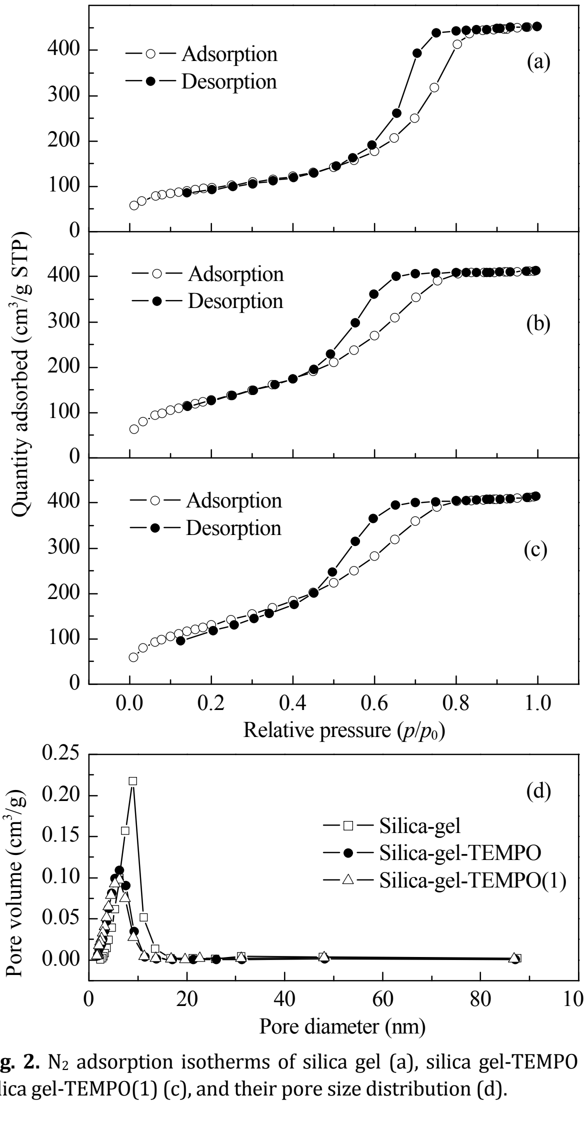


Fig. 2. N_2 adsorption isotherms of silica gel (a), silica gel-TEMPO (b), silica gel-TEMPO(1) (c), and their pore size distribution (d).

Table 2
Physical data of catalysts.

Catalyst	BET surface area (m^2/g)	Pore volume ^{a} (cm^3/g)	Average pore diameter ^{b} (nm)
Silica gel	348	0.71	6.9
Silica gel-TEMPO	477	0.66	4.5
Silica gel-TEMPO(1)	486	0.67	4.3

^{a} Pores with diameters between 1.7 and 300 nm.
^{b} BJH adsorption average pore diameter (4V/A).

3.2.2. Textural and morphological characteristics and adsorption characterization

The N_2 adsorption isotherms of the materials confirmed the structural quality of the supported silica gel-TEMPO as compared to that of its parent silica gel (Fig. 2). The isotherms were type IV [31], which exhibited the characteristics of mesoporous materials with a disordered pore structure. The hysteresis loops of the samples are H1 type according to the classification of hysteresis loops by IUPAC [32], which is associated with porous materials exhibiting a narrow distribution of relatively uniform cylindrical pores. These uniform pores provide room for NO_x adsorption and alcohol oxidation. The specific surface area, mesopore diameter, and average cumulative pore volume (V_{BJH}, $4V/A$) of the samples are presented in Table 2. After the silica gel was immobilized with TEMPO, the pore volume of silica gel-grafted TEMPO decreased from 0.71 to 0.66 cm^3/g, and the average pore diameter decreased from 6.9 to 4.5 nm. These changes suggested that TEMPO was immobilized onto silica successfully. Conversely, the surface areas of the samples, which followed an opposite trend (ranging from 348 to 477 m^2/g), can be explained by that silica gel particles were broken into smaller sizes, yielding an increase in surface area. The pore volume of silica gel-TEMPO and silica gel-TEMPO(1) almost did not change, which showed that very little TEMPO was lost from the silica gel and the catalyst physical characteristics were also not affected by the oxidation reaction. The average pore diameter of silica gel-TEMPO and silica gel-TEMPO(1) was 4.5 and 4.3 nm, respectively, which was evidence that there was NO_x residue in the one-time used catalyst.

NO_x-TPD was employed to measure the NO_x adsorption quantity. The amount of desorbed NO_x of the samples was calculated based on desorption peak area. As shown in Fig. 3, the desorption curve of silica gel-TEMPO exhibited its desorption capacity is 0. The desorption curve of silica gel-TEMPO-NO_x was flat in the purge phase at room temperature Fig. 3(b)), which suggested that physically adsorbed NO_x had been discharged. The adsorbed NO_x amount was 0.357 mmol/g (Table 3), which agreed with the result from the elemental analysis in order of magnitude. The NO_x-TPD curve of silica gel-TEMPO(1) (Fig. 3(c)) shows that even when once used, 0.160 mmol/g NO_2 (Table 3, parts of the gas was lost before entering the detector) was still left in the channels. This observation is important for interpreting the catalytic mechanism of the alcohol oxidation reaction.

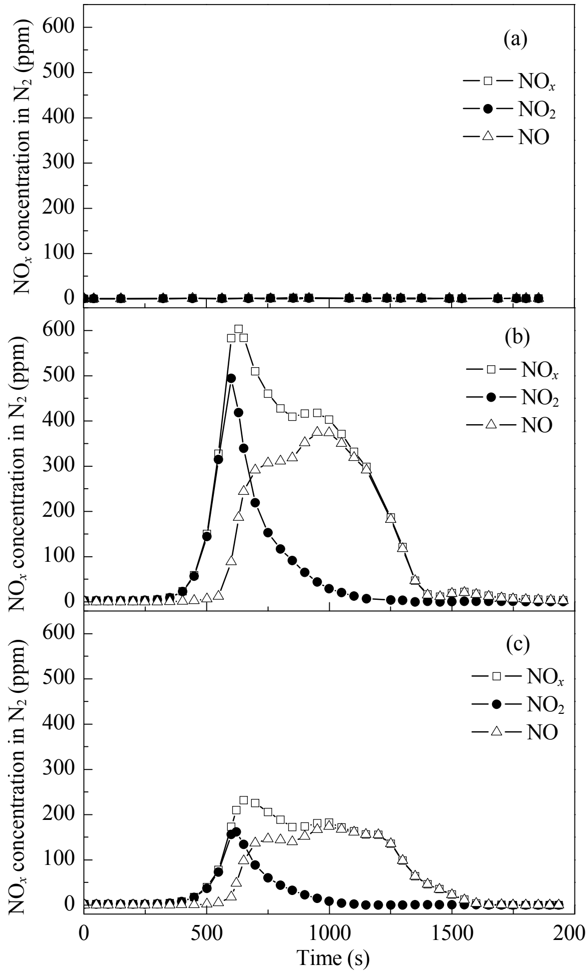


Fig. 3. NO_x-TPD profiles of silica gel (a), silica gel-TEMPO-NO_x (b), and silica gel-TEMPO(1) (c).

3.3. Aerobic oxidation of alcohols by silica gel-supported TEMPO-NO_x

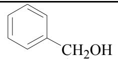
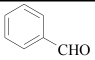
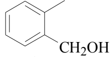
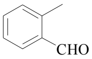
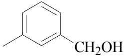
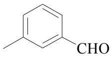
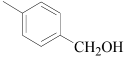
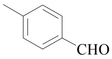
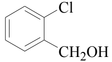
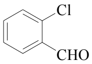
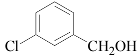
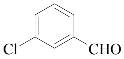
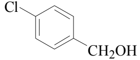
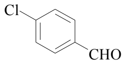
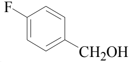
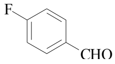
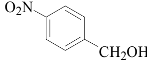
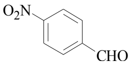
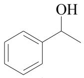
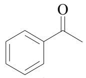
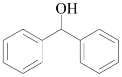
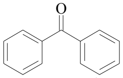
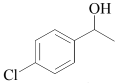
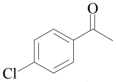
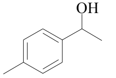
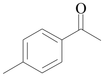
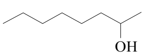
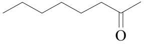
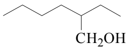
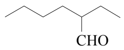
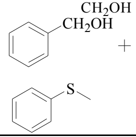
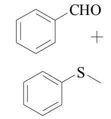
To test the catalytic activity of the silica gel-supported TEMPO-NO_x system in the oxidation of alcohols (Table 4), the reaction conditions were first optimized using benzyl alcohol as a model substrate. Benzyl alcohol was readily oxidized to benzyldehyde with 100% conversion and > 99% product selectivity in the presence of 0.5 g silica gel-supported TEMPO/NO_x. This catalytic system was applied to oxidize various types of benzylic aliphatic alcohols into their corresponding aldehydes and ketones, and the results are listed in Table 4. Most benzylic alcohols can be oxidized to their corresponding aldehydes within 2 h with 99% conversion and selectivity as high as 99%, while a little difference was observed between some electron-rich and electron-deficient benzylic alcohols. (Table 4, entries 2–4, 2.5 h; entry 9, 3.5 h). It is worth mentioning that

Table 3
NO_x amount from different samples.

Catalyst	NO (mmol/g)	NO_2 (mmol/g)	NO_x (mmol/g)
Silica gel-TEMPO ^{a}	0	0	0
Silica gel-TEMPO-NO_x ^{b}	0.237	0.120	0.357
Silica gel-TEMPO(1)	0.121	0.039	0.160

^{a} Before NO_x adsorption.
^{b} After NO_x adsorption.

Table 4
Aerobic oxidation of alcohols using silica gel-supported TEMPO-NO_x[a].

Entry	Substrate	Product	Time (h)	Convertion[b] (%)	Selectivity[c] (%)
1			2	>99	>99
2			2.5	>99	98
3			2.5	>99	>99
4			2.5	>99	>99
5			2	>99	>99
6			2	>99	>99
7			2	>99	>99
8			2	>99	>99
9			3.5	>99	>99
10			2	>99	>99
11			2	>99	>99
12			2	>99	>99
13			12	97	>99
14			5	98	>99
15			6	>99	92
16[d]			2	>99	>99

[a] All reactions were carried out according to the procedure in Section 2.3.
[b] Conversion and selectivity are based on GC with area normalization.
[c] Selectivity refers to the products aldehyde and ketone.
[d] Only benzyl alcohol was oxidized.

the system also showed high activity in oxidizing various secondary alcohols to their corresponding ketones (Table 4, entries 10–14). 2-Octanol can be oxidized to 2-octyl ketone with 98% of conversion in only 5 h. The oxidation of an aromatic secondary alcohol with an electron-donating group on the benzene ring (Table 4, entry 12) was easier than that with an electron-withdrawing group (Table 4, entry 13) on the benzene ring under the reaction conditions. The oxidation of benzyl alcohol (1 mmol) together with sulfide (1 mmol) (Table 4, entry 16) was also studied. After 2 h, most of the benzyl alcohol (>99%) was transformed into benzyl aldehyde, and only a little amount of sulfide (<1%) was converted. This clearly indicates that this catalytic system can selectively oxidize alcohols mixed with sulfides.

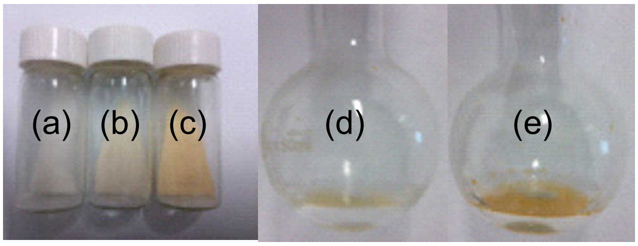
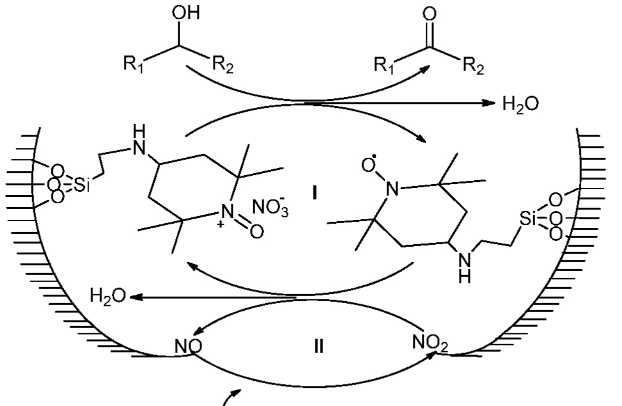


Fig. 4. Pictures of silica gel (a), silica gel-TEMPO (b), silica gel-TEMPO-NO_x (c), and the reaction mixture of started (d) and completed (e) reaction.

We also found an interesting phenomenon in the oxidation process. The transparent white silica gel (Fig. 4(a)) turned light yellow when grafted with TEMPO (Fig. 4(b)), and then changed to orange after adsorbing NO_x (Fig. 4(c)). When the catalyst was added into an alcohol CH_2Cl_2 solution, it turned light yellow again (Fig. 4(d)). However, as the reaction proceeded, the color of the silica gel changed to be orange gradually. In general, the catalyst in the reaction mixture after the oxidation reaction looked like that before it was added into the flask (Fig. 4(e)). The oxidation process can be illustrated as Scheme 3. White silica gel with immobilized TEMPO turns light yellow because of the color of TEMPO. After NO_2 adsorption, the immobilized TEMPO was oxidized to $TEMPO^+NO_3^-$ (cycle I). Meanwhile, NO_2 was reduced to NO (cycle II), which was reoxidized by O_2 that diffused into the pores from the air in the atmosphere. Thus the silica pores were filled with NO_x, and the catalyst was orange. When reaction began, alcohol was oxidized by $TEMPO^+NO_3^-$ to the corresponding aldehyde or ketone, and at the same time, $TEMPO^+NO_3^-$ was reduced to TEMPOH, which entered the next cycle. When the oxidation process was completed, only orange $TEMPO^+NO_3^-$ and NO_x remained in the catalyst. The color changes in the oxidation process can be explained that the silica has enough mechanical strength and does not break under magnetic stirring, so NO_x will remain stored in the silica pores after reaction, and the catalyst can be reused without a second NO_x adsorption. This is another advantage of this catalytic system.



Scheme 3. Proposed oxidation mechanism of alcohol oxidation catalyzed by silica gel-supported TEMPO-NO_x.

Graphical Abstract

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Silica gel-supported TEMPO with adsorbed NO$_x$ for selective oxidation of alcohols under mild conditions

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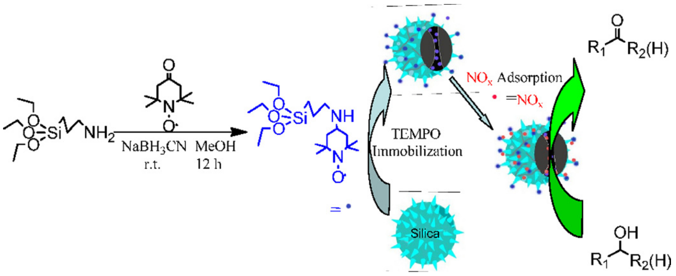

The gas-solid one body catalyst, silica gel-TEMPO-NO$_x$, was prepared by immbolizing TEMPO on silica gel and then absorbing NO$_x$. Silica gel-TEMPO-NO$_x$ expressed good performance in the selective oxidation of alcohols under mild conditions.

4. Conclusions

Silica gel-supported TEMPO was prepared by grafting the SPE padding silica gel surface with 3-(triethoxysilyl) propamino-TEMPO. The resulting material in combination with NO$_x$ was used in alcohol oxidation. It was found that various kinds of alcohol substrates, including benzylic alcohols, secondary aliphatic, and aromatic alcohols, were oxidized to the corresponding aldehydes and ketones with high conversions and selectivities at atmospheric atmosphere and room temperature.

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