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The stability of covalently immobilization of TEMPO on the polymer surface through ionic liquid linkage: a comparative and model research

Abstract: Covalently immobilizing the active sites or ligands on a polymer surface is an efficient strategy to achieve a full use of expensive organic parts. In this work, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was anchored onto polystyrene beads through an ether bond or an ionic liquid bridge. We quantitatively compared their thermal stabilities at nitrogen atmosphere and their chemical stabilities in a biphasic oxidation surrounding. It was found that the ionic liquid-bridged TEMPO exhibited an additional advantage of stability and could be reused for 30 consecutive recycles with a conversion ratio above 90% without any significant loss under the condition of the Montanari oxidation system (NaClO/NaBr, CH₂Cl₂/water), and the overall reaction time exceeded 2700 min.

Keywords: alcohols; heterogeneous catalyst; ionic liquid; recyclability; stability.

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1 Introduction

Catalysts have been employed extensively for chemical reactions. However, the efficient separation and subsequent recycling of homogeneous catalysts remain a scientific and engineering challenge. One of the effective ways to overcome this problem is the use of heterogeneous catalysts, which have profound advantages of straightforward

recovery and could be reused from the reaction mixture by simple filtration, decantation, and magnetic alterations (1, 2). A small molecule catalyst can be immobilized on several insoluble supports such as organic polymers (3–7), silica sol-gels (8, 9), and mesoporous silica (10–12). Organic polymer supports have attracted extensive interest, owing to their various characteristics, ease of functionalization, and well-controlled morphology.

Chemoselective oxidation of alcohols to carbonyl compounds is an important reaction in organic synthesis (13). In order to achieve economic and environmental benefits, the use of metal-free catalysts for selective oxidation of organic compounds has been attracting much attention (14–17). Stable free nitroxyl radicals, typically 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), play an important role in this area (18–22). However, the isolation of TEMPO from the reaction mixture or products needs a tedious procedure. To simplify the process of product purification and catalyst recovery, the immobilized/supported TEMPO catalyst seems to be a good alternative. Recently, TEMPO has been immobilized onto inorganic (23–25) as well as organic (26–30) supports, affording solid catalysts, which were readily separated from the reaction mixtures and recovered by filtration, dried under vacuum, and reused without any further treatments. These solid catalysts were developed because of their easy separation and possibility for use as a fixed-bed reactor (31).

Polystyrene is the most used organic polymer support because, despite its facile modification, it can be fabricated into particles with various sizes (nano, micro, or milli) and shapes (solid, porous) and can be cross-linked to a certain degree. In our earlier studies (32, 33), nitroxyl radical TEMPO was grafted directly to a magnetic polystyrene nanosphere through an ether bond. This catalyst was effective in the selective oxidation of a number of primary and secondary alcohols. Ionic liquids (ILs) have attracted considerable attention over the last decade, owing to their dramatic effect on the observed conversion and selectivity, and have been called “designer solvents” (34). The immobilization of ILs facilitates the separation process and reduces the cost of the process when a smaller amount of IL is employed (35, 36). Zhu et al. (37) reported a recyclable catalyst bearing an IL-supported TEMPO and

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iodoarene moieties used for alcohol oxidations in high yields under mild conditions. Beejapur et al. (38) developed a recyclable catalyst for alcohol oxidation based on an imidazolium-tagged TEMPO catalyst adsorbed on an imidazolium-modified support or on an unmodified silica gel with high recyclability.

So far, several strategies have emerged to address the problem of decreased activity of TEMPO through the design of various types of supported TEMPO, including the use of soluble support and magnetic nanoparticles (39–42). However, previously, the stability of heterogeneous catalysts has not been reported specifically. Herein, we developed a catalyst-immobilizing TEMPO moiety via the covalent immobilization of ILs to polystyrene beads. Then we quantitatively compared their thermal stabilities in nitrogen atmosphere and their chemical stabilities in a biphasic oxidation surrounding.

2 Experimental

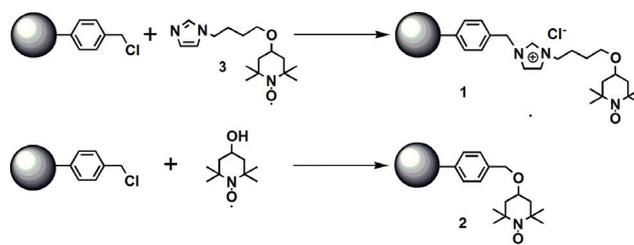
2.1 Materials

All reagents were analytical grade and used as purchased without further purification. 4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl(4-OH-TEMPO), benzyl alcohol were bought from Sigma-Aldrich Co (Shanghai, China); imidazole, tetrabutylammonium hydrogen sulfate (Bu_4HSO_4), and sodium hypochlorite (NaClO , active chlorine 13%) were purchased from Aladdin Industrial Inc (Shanghai, China); NaOH , NaCl , NaHCO_3 , NaBr , MgSO_4 , ethyl acetate, petroleum ether, toluene, and CH_2Cl_2 were obtained from Huadong Medicine Co., Ltd (Hangzhou, China).

2.2 Preparation and characterization

2.2.1 PS-IL-TEMPO 1

The functional moiety **3** (Scheme 1) was synthesized according to the work of Song et al. (43). Into a solution of $\text{Br}(\text{CH}_2)_4\text{Br}$ (19.5 g, 90 mmol) in THF (15 ml), Bu_4HSO_4 (0.4 g, 1.2 mmol) was added, followed by 4-OH-TEMPO (1.7 g, 30 mol) and an aqueous of NaOH (50 wt%, 7 ml). The reaction mixture was stirred overnight at room temperature. After that, the mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with saturated sodium chloride aqueous solution, dried over anhydrous MgSO_4 ,



Scheme 1 Synthesis of the PS bead-supported catalysts.

evaporated by rotary evaporation in vacuum, and isolated by a silica column (petroleum ether and ethyl acetate 8:1), giving a red viscous oil-like product ($\text{Br}(\text{CH}_2)_4\text{-O-TEMPO}$). The product was characterized by GC/MS.

And then, Bu_4HSO_4 (0.67 g, 2 mmol) was added into a solution of $\text{Br}(\text{CH}_2)_4\text{-O-TEMPO}$ (15.4 g, 50 mmol) in THF (10 ml), followed by imidazole (10.2 g, 150 mmol) and an aqueous of NaOH (50 wt%, 12 ml). The mixture was vigorously stirred overnight at room temperature. After that, the mixture was poured into cold water. The aqueous phase was extracted by ethyl acetate for three times. The organic phases were merged and washed with saturated sodium chloride aqueous solution. After that, the organic solution was dried using anhydrous MgSO_4 . The dried solution was evaporated by rotary evaporation in vacuum and then isolated by a silica column (dichloromethane/methanol 9:1), providing a red viscous oil **3**. The product was characterized by GC/MS.

Chloromethylated polystyrene beads (7.0 g, 31.4 mmol Cl, DVB 7%; average particle size: 280 μm) were swelled in toluene (25 ml) before the addition of **3** (9.2 g, 31.4 mmol). Then the reaction mixture was stirred for 48 h at 80°C under an atmosphere of nitrogen. The solid material was collected by filtration and washed three times with acetone and three times with distilled H_2O . The solid was immersed in ethyl alcohol for 12 h and dried in vacuum at 45°C. The product was characterized by FTIR and elemental analysis.

2.2.2 PS-TEMPO 2

Chloromethylated polystyrene beads (7.0 g, 31.4 mmol Cl, DVB 7%; average particle size: 280 μm) were swelled in toluene (25 ml) before the addition of 4-hydroxy-TEMPO (5.4 g, 31.4 mmol). The reaction mixture was stirred for 48 h at 80°C under an atmosphere of nitrogen. The solids were collected by filtration, washed three times with acetone and three times with distilled H_2O , and then immersed in ethyl alcohol for 12 h and dried in vacuum at

45°C. The product was characterized by FTIR and elemental analysis.

2.2.3 Characterizations

FTIR spectra (200–4000 cm^{-1}) were recorded by diffuse reflectance using a Nicolet iS10 Fourier transformation infrared spectrophotometer. The particle samples were pressed into a KBr disk, and then the spectra were recorded. Thermal stability measurements of these catalysts were carried out on a NETZSCH TG 209 F3 Tarsus thermal analyzer, and the samples were heated in nitrogen at a constant heating rate of 10°C/min from 30°C to 700°C (kept at 105°C for 10 min). XPS scan was run to determine the composition of N atoms present at the surface of catalysts before and after oxidation.

2.2.4 Alcohol oxidation

2.2.4.1 General procedure

Catalyst **1** or **2** (5% mol), benzyl alcohol (0.3 g, 3.0 mmol), and dichloromethane (7.5 ml) were added in a 50-ml round-bottom flask. The mixture was stirred for 0.5 min, and 0.4 mol/l of NaClO (11.2 ml, 4.5 mmol, pH 9.1) and 1 mol/l of NaBr (0.3 ml, 0.3 mmol) were added sequentially, and the mixture was stirred at room temperature. After 90 min, the reaction was quenched by destroying the excess hypochlorite with saturated sodium sulfite solution (7.5 ml), and the catalyst particles were then collected by filtration. The reaction medium was carefully decanted for GC/MS analysis, and the particles were washed two times with distilled water and two times with CH_2Cl_2 , and then the catalyst was reused for the next cycle without drying or further activation.

3 Results and discussion

3.1 FTIR analysis

The FTIR spectrum (Figure 1) of PS-IL-TEMPO shows that the typical peaks at 680 and 1265 cm^{-1} corresponding to the functional group $-\text{CH}_2\text{Cl}$ disappeared, while new peaks appeared at 1630, 1360, 1200, and 1150 cm^{-1} , which were attributed to the presence of quaternized imidazole, N-O, C-N, and C-O bond, respectively. These evidences proved that the IL and TEMPO moiety were successfully grafted to the support polymer.

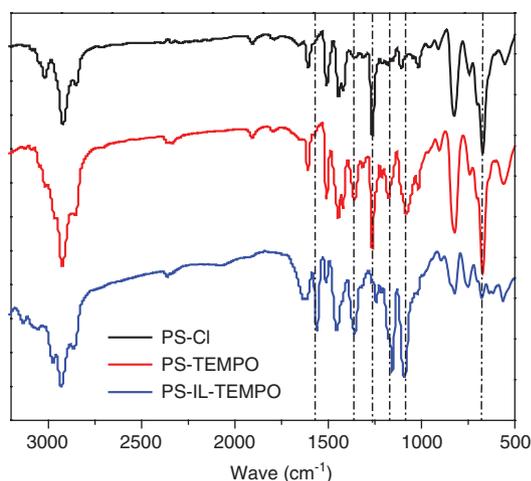


Figure 1 FTIR spectra of PS-Cl, PS-TEMPO, and PS-IL-TEMPO.

3.2 Thermal and application stability study

3.2.1 Thermal stability

The thermal stability of the samples was investigated by thermogravimetric analysis (TGA). The TGA curves of PS-Cl, PS-TEMPO, and PS-IL-TEMPO are shown in Figure 2. The loss of PS-Cl began slowly at 300°C, which was attributed to the degradation of $-\text{CH}_2\text{Cl}$, and the second loss at around 450°C was related to the degradation of the main polymer (44–46). However, the weight loss of PS-TEMPO started at around 150°C and that of PS-IL-TEMPO at around 200°C was mostly attributable to the decomposition of the grafted chain. It can also be determined that the weight of PS-IL-TEMPO decreased significantly within 300°C, and the weight loss was twice that of PS-TEMPO. This is possibly ascribed to the decomposition of the

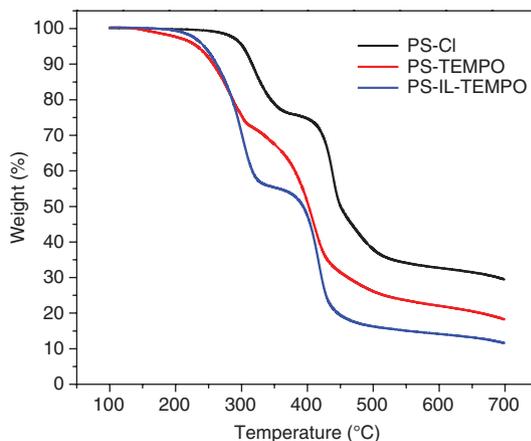


Figure 2 TGA curves of PS-Cl, PS-TEMPO, and PS-IL-TEMPO.

long chain attached to the polystyrene beads, including $-CH_2-$ and **3** (Scheme 1). This conclusion was verified by calculation; the maximum weight loss peaked at 300°C for PS-IL-TEMPO and at 270°C for PS-TEMPO, respectively. The stability of PS-TEMPO decreased owing to the presence of the TEMPO group; this reduction may be ascribed to steric hindrance. The steric hindrance, caused by the close distance of the ether bond with the benzene ring, deviated the chemical bond from the normal angle, thus forming an intermolecular tension that made the bond unstable. In contrast, the uneven electronic distribution of C-O may be another reason for the reduced stability of chlorine methyl.

3.2.2 The study of application reusability

The advantages of the PS-IL-TEMPO catalyst lie in the facile separation and recyclability. It can be conveniently recycled within seconds, followed by washing thoroughly with H_2O and CH_2Cl_2 , in that order. A second run was performed by adding fresh benzyl alcohol, NaClO, and NaBr under the same experimental conditions. This catalytic system was stable and efficient for 30 cycles without significant loss of catalytic capability, as shown in Figure 3. The PS-IL-TEMPO catalyst showed high reusability for alcohol oxidation at room temperature. For the PS-TEMPO catalyst, as shown in Figure 4, the activity was decreased after five cycles with a conversion ratio below 90%. The selectivity of these catalysts was all above 99%. The drop in activity was possibly due to TEMPO moiety loss caused by the breakage of the ether bond, which may be effected by ClO^- and BrO^- .

This result is similar to that of our previous work (32). The PS-IL-TEMPO catalyst showed high stability against

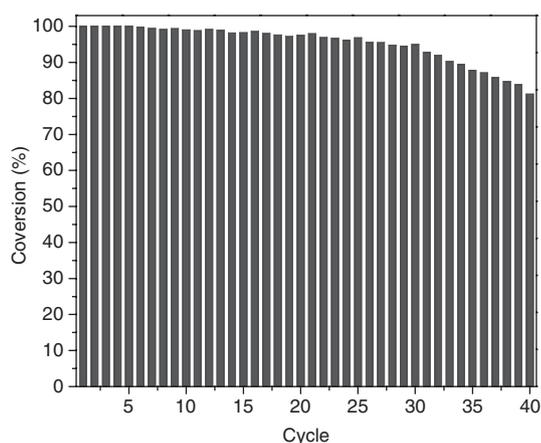


Figure 3 Recyclability of PS-IL-TEMPO in the oxidation of benzyl alcohol (conversion and selectivity were determined by GC/MS).

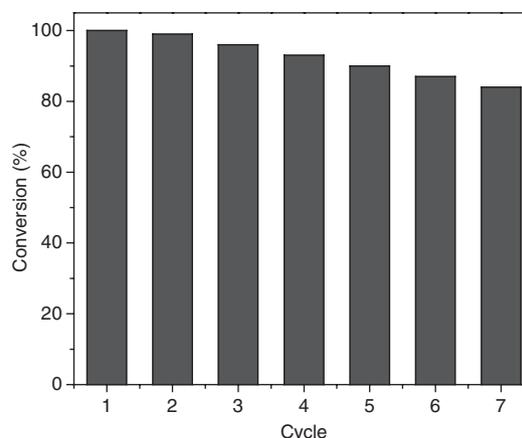


Figure 4 Recyclability of PS-TEMPO in the oxidation of benzyl alcohol (conversion and selectivity were determined by GC/MS).

the active species rupturing into liquid phase under the given reaction condition. The presence of alkaline imidazolium provided a site that could capture and transmit ClO^- and BrO^- , formed a microenvironment, and minimized the interaction force between TEMPO and the surface of the support polymer. In addition, the presence of IL possibly increased the flexibility and mobility of the functional group and prevented the chemical bond from fracturing (47).

3.3 Surface analysis of the catalysts

The variation of the surface composition on the PS bead-supported catalyst was detected by XPS.

XPS provides valuable information about the surface structural variation occurring after oxidation reaction (48, 49). The C1s (C-C) peak at 284.6 eV was used to calibrate the binding energy scale. In order to obtain detailed information, a narrow scan of the N1s region for the catalysts PS-TEMPO and PS-IL-TEMPO was conducted to determine the type of linkage and the amount of nitrogen. According to the mechanism of alcohol oxidation (16, 50, 51), the transformations occurred via $TEMPO^+$, which was generated by the oxidation of TEMPO; after the reaction with the primary or secondary alcohol, $TEMPO^+$ reverts to TEMPO. Figure 5 shows narrow spectra for N1s for the PS-TEMPO catalyst; the characteristic emission peaks at 401 and 406 eV reveal the presence of TEMPO and $TEMPO^+$ on the surface of PS, respectively. The presence of $TEMPO^+$, as shown in Figure 5, may have been caused by the support polymer, which prevented the transfer of alcohol. But for the PS-IL-TEMPO catalyst, as shown in Figure 6, $TEMPO^+$ disappeared completely, which may have been caused by

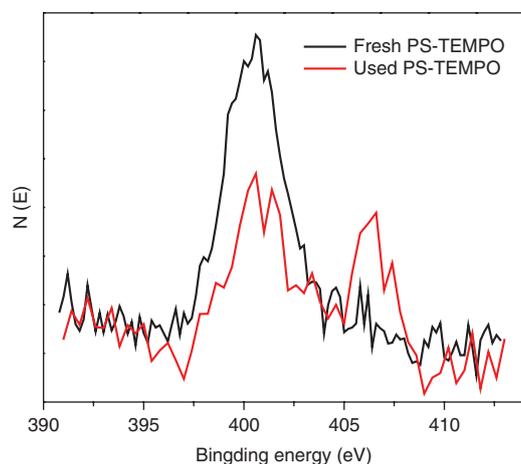


Figure 5 N1s narrow scan of XPS analysis for PS-TEMPO.

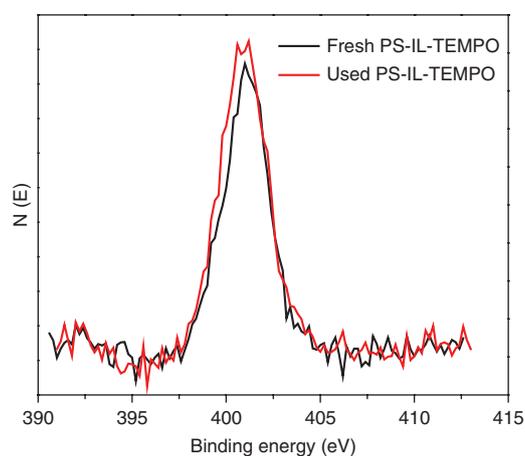


Figure 6 N1s narrow scan of XPS analysis for PS-IL-TEMPO.

the presence of IL, which provided alcohol for TEMPO⁺ and promoted the reaction.

4 Conclusions

We firstly prepared a polystyrene bead-supported TEMPO catalyst via covalent immobilization through an ionic liquid bridge and quantitatively compared their stabilities in different atmospheric and oxidation conditions. The ionic liquid linker not only supplied a facile covalent point for grafting TEMPO, but also gave the catalyst excellent performance owing to the supply of a proper surface surrounding to let the aqueous and organic phases fully contact the interfaces. The obvious negative loss of the PS-IL-TEMPO catalyst after 30 consecutive cycles indicated a possibility for using this catalyst in a long-term batch

reactor. Further studies on the use of a fixed-bed reactor to extend the application of this catalyst are currently being carried out.

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