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Synergistic Catalysis within the TEMPO-Functionalized Periodic Mesoporous Organosilica with Bridge Imidazolium Groups in the Aerobic Oxidation of Alcohols

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Anchoring 2,2,6,6-tetra-methylpiperidine-1oxyl radical (TEMPO) within the nanospaces of a periodic mesoporous organosilica with bridged immidazolium group led to an unprecedented poweful bifunctutional catalyst (TEMPO@PMO-IL-Br), which showed enhanced activity in the metal-free aerobic oxidation of alcohols. The catalyst and its precursors were characterized by N_2 adsorption-desorption analysis, transmission electron microscopy (TEM), small angle X-ray scattering (SAXS), thermal gravimetric analysis (TGA), diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), solid state electron paramagnetic resonance (EPR) spectroscopy, elemental analysis, transmission electron microscopy (TEM) and high resolution TEM. It was clearly found that the catalytic activity of of SBA-15-functionalized TEMPO (TEMPO@SBA-15) not bearing IL, TEMPO@PMO-IL-Cl, PMO-IL-AMP, or individual catalytic functionalities (PMO-IL/ TEMPO@SBA-15) was inferior as compared with those obtained from TEMPO@PMO-IL-Br in the metal-free aerobic oxidation of benzyl alcohol, suggesting the critical role of co-supported TEMPO and imidazolium bromide in obtaining high catalytic activity in the described catalyst system. Our observation clearly points to the fact that the combination of imidazolium bromide units in the close proximity of TEMPO moieties in the nanospaces of TEMPO@PMO-IL-Br might be indeed one of the key factor explaining the enhanced catalytic activity observed for this catalyst in oxidation of benzyl alcohol possibly through a synergistic catalysis relay pathway. A proposed model was suggested for the observed synergistic effect.

Introduction

In the past decades imidazolium-based ionic liquids have received increasing attention due to their unique properties related to very low vapour pressure, the capability to dissolve both organic and inorganic reactants, and tuneable structure and polarity. In this context, significant advances have been achieved in the application of ionic liquid (ILs) as potential green replacement media for volatile organic solvents in organic synthesis and homogeneous catalysis.[1] In particular, the significance of using functionalized ionic liquid (so called task specific IL, TSIL) has been well drawn in various types of chemical transformations and organic synthesis under homogeneous reaction conditions.[2] Among all the systems, the use of imidazolium ionic liquid functionalized with 2,2,6,6-tetra-methylpiperidine-1oxyl (TEMPO) is recognized as an effective approach for the selective aerobic oxidation of alcohols in combination with $NaNO_2$ as co-catalyst.[3, 4] In these studies, $NaNO_2$ was thought to be a NO-source while halide

counter ion of imidazolium IL provided the necessary Br_2/Br^- redox couple in order to ensure fast electron transfer from alcohol to molecule oxygen through a catalysis relay mechanism.[4] However, several drawbacks like, high cost, evidence of toxicity even at low concentration,[5] unsuitable viscosity and tedious separation procedure hinder the widespread applications of homogeneous ionic liquid systems. For these reasons, the use of ionic liquids as homogeneous reaction media is often debatable from the view point of green and sustainable chemistry. Hence, in order to avoid the intrinsic disadvantages of using homogeneous ionic liquids, their efficient heterogenization is highly desirable because it considerably reduces the amount of expensive ILs while allowing easy separation and recycling of both IL reaction media and utilized catalyst system from the reaction products. Inspired by the synergistic effect of ionic liquids in TEMPO-catalyzed selective alcohol oxidation,[3] the possibility of designing novel catalyst system with improved catalytic activity by an appropriate combination of IL/TEMPO system on a suitable support which enable efficient recycling of both system have been described.[6] It was suggested that the high synergism in these IL/TEMPO Supported systems is most likely caused by the confinement of bromide counter ion of IL in the close spatial proximity of immobilized TEMPO in the same support.[6] What is appealing in these systems is that the described synergistic effect produces immediately a much better catalytic activity and/or selectivity in comparison with

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their individual counterpart.[6] Although, the high cost of homogeneous TEMPO, can be avoided to a great extent by these systems, in most cases the use of non-covalent IL in the form of physisorbed (*release and catch system*) is potentially restricting the efficient IL recovery. We have recently engaged in developing several periodic mesoporous organosilica (PMO) with extraordinary robust bridged imidazolium network so called PMO-IL. These material was found to be excellent supported reaction media and/or versatile support for immobilization and stabilization of varied transition metal nanoparticles, in several important synthetic transformation.[7] With much compelling evidences, it was shown that these functional catalysts combines the molecular diversity of the IL-like structures with highly durable catalytic activity of metal catalysts in a single solid. Considering the excellent synergy in combining the IL with TEMPO, we wondered whether the covalent immobilization of TEMPO onto the surface of PMO-IL in close proximity of bridged imidazolium group might not only amplify the catalytic performance of the supported TEMPO but it can also combine the advantages of employing molecular oxygen through a catalysis relay approach with the possibility of recycling both IL and TEMPO at the same time.

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Results and Discussion

To realize this hypothesis, PMO-IL was initially prepared by hydrolysis and co-condensation of 1,3-bis(3-trimethoxysilylpropyl)imidazolium chloride and TMOS in the presence of Pluronic P123 as a template under acidic conditions according to our previously reported procedure.[7,8] The resulting PMO-IL were then allowed to react with (3-aminopropyl) trimethoxysilane followed by reductive amination with 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy (4-oxo-TEMPO) in the presence of $NaBH_3CN$ to furnish the corresponding PMO-IL-supported TEMPO (TEMPO@PMO-IL-Cl) (Scheme 1).
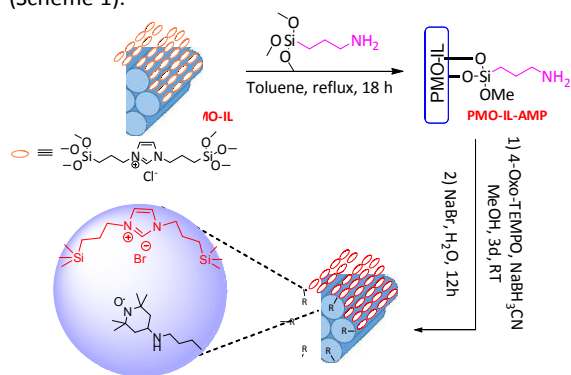

Scheme1. Schematic pathway for the preparation of TEMPO@PMO-IL-Br.

Since the catalytic activity of supported TEMPO can remarkably be relied on the synergy of anionic part of IL-like bridged imidazolium groups, the anion Cl^- was exchanged using

a saturated aqueous solution of NaBr to afford the corresponding catalyst TEMPO@PMO-IL-Br.[8]

The N_2 adsorption analysis for all materials (PMO-IL, PMO-IL-AMP and TEMPO@PMO-IL-(Br)) showed a typical type-IV isotherm pattern with a sharp hysteresis loop at P/P_0=0.6-0.8, which is characteristic of highly ordered mesoporous materials with narrow pore size distribution and 2-dimensional hexagonal pore structure (Figure 1).
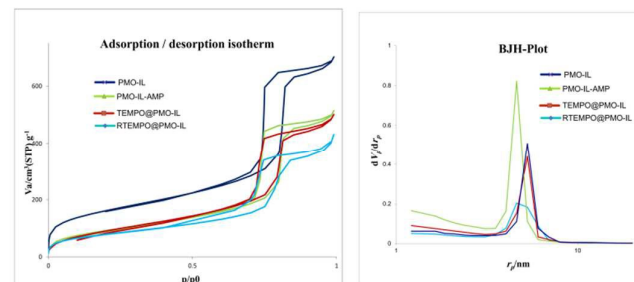
Figure 1. N_2 adsorption–desorption isotherms (left) and BJH pore size distribution (right) of PMO-IL (dark blue), PMO-IL-AMP (green) and TEMPO@PMO-IL-Br (red), and recovered TEMPO@PMO-IL-Br (blue)
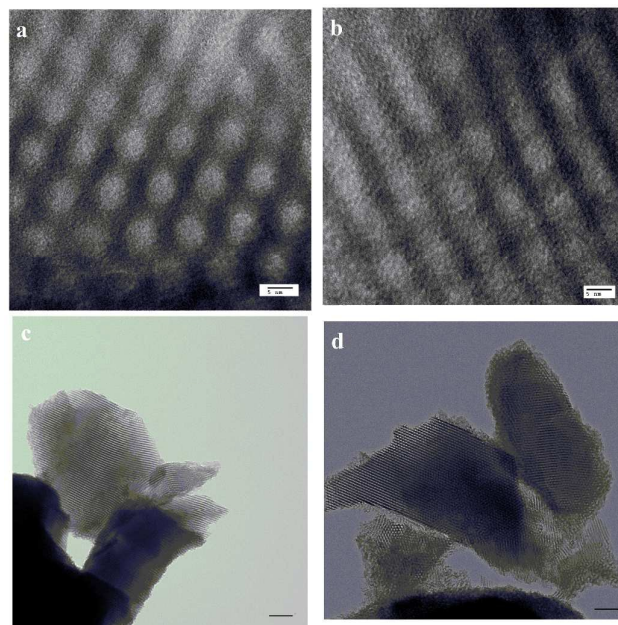
Total pore volume and pore diameter was estimated by measuring the volume of nitrogen adsorbed at P/P_0=0.99 and BJH model based on the adsorption branch of the isotherms, respectively. PMO-IL has a BET surface area of 578.8 m^2g^{-1}, a regular pore diameter of 10.6 nm and a total pore volume of 1.08 cm^3g^{-1}. By comparing of nitrogen adsorption analysis data of TEMPO@PMO-IL- with PMO-IL itself, surface area and pore volume decrease to 351 m^2g^{-1} and 0.77 cm^3g^{-1}, respectively. These results confirmed to some extent that the organic moieties were successfully grafted inside the mesochannels. Furthermore, the IR spectrum of TEMPO@PMO-IL(Br), beside the signals that are characteristic of alkylimidazolium groups [3125 cm^{-1} (for unsaturated C-H stretching), 3050, 2918 cm^{-1} (aliphatic C-H stretching), 1620 cm^{-1} (C=N stretching of imidazolium ring), 1558 cm^{-1} (C=C stretching of imidazolium ring), 1442 cm^{-1} (C-H deformation vibrations), 700-790 cm^{-1} (for C-Si stretching vibrations)], exhibits a new band at 1348 cm^{-1} which is reasonably related to the N-O free radicals (Figure 2).[9]
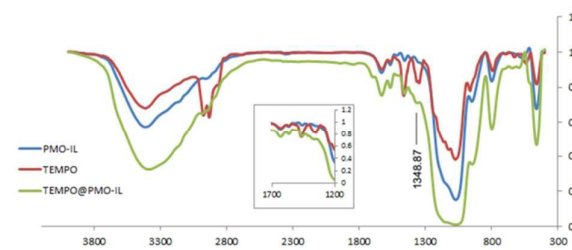
Figure 2. FT-IR spectroscopy of PMO-IL, TEMPO and TEMPO@PMO-IL-Br.

This clearly indicated successful loading of TEMPO on the surface of PMO-IL. This statement was further supported by elemental analysis (CHN analysis) and thermogravimetric analysis (TGA), estimating the loading of TEMPO and IL group
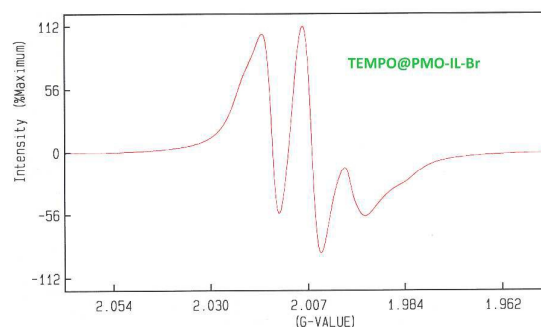
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at 0.25 and 0.98 mmol g^{-1}, respectively (Figure S3-S5, ESI). Moreover, TEM images of TEMPO@PMO-IL clearly show highly ordered cylindrical pores with uniform size, which is in good agreement with the results obtained from N$_2$-adsorption-desorpsion analysis (Figure 3). The additional structural information about TEMPO@PMO-IL-Br was obtained by small angle X-ray scattering (SAXS) and solid state electron paramagnetic resonance (EPR) spectroscopy. The SAXS patterns exhibited three reflections indexed as (100), (110), and (200) according to the highly ordered 2D hexagonal mesostructures (*P6mm* space group, Figure S6).

Figure 4. Solid state EPR spectrum of TEMPO@PMO-IL-Br

Figure 3. a, b) HRTEM images TEMPO@PMO-IL-Br before and after recycling from the aerobic oxidation of benzyl alcohol respectively (scale bar: 5 nm); c, d) TEM images of TEMPO@PMO-IL-Br with low magnification (scale bar: 100 nm) before and after recycling from the aerobic oxidation of benzyl alcohol respectively

The solid state EPR spectrum showed a triplet with a *g* value at ≈ 2.007, which is very close to that of sol-gel entrapped TEMPO.[10] This spectra strongly confirms the presence of N-O radical moiety in TEMPO@PMO-IL-Br (Figure 4, please also see: Figure S7, S8).

We first tested the catalytic activity of PMO-IL-TEMPO in the aerobic oxidation of benzyl alcohol as a model substrate, in the presence of molecular oxygen in combination with varied NO$_x$ sources (Table 1). In this regard, this study aims at identifying whether imidazolium groups in close proximity of TEMPO inside the nanospaces of our catalyst system in combination with NO/NO$_2$ may cooperatively bridge the large kinetic gap between O$_2$ and TEMPO.[11]

To assign the optimal experimental conditions, the impact of various nitrite sources such as *tert*-butylnitrite (TBN) and NaNO$_2$ in different solvent such as water, toluene, water/acetic acid (50 mol%), toluene/acetic acid (50 mol%) and pure acetic acid were examined. Our initial investigations showed that in the presence of TEMPO@PMO-IL-Br (0.75 mol%) and atmospheric pressure of O$_2$ (622 Torr) in combination with either NaNO$_2$ or TBN, the oxidation of benzyl alcohol was quite inefficient (Table 1, entries 1-5). Although the conversion was improved to some extent by decreasing the volume of water no yield better than 27% was obtained (Table 1, entry 5). A more or less the same result was observed by employing NaNO$_2$ in toluene under otherwise the same reaction conditions (Table 1, entries 6, 7). However, a considerable improvement was achieved when TBN (instead of NaNO$_2$) with a little bit more AcOH (30 mg) as additives were employed and a benzaldehyde yield up to 40% was obtained (Table 1, entries 8, 9). Notably, no significant oxidation of benzyl alcohol in the absence of TBN, TEMPO@PMO-IL-Br or AcOH occurred under the same reaction conditions (Table 1, entries 10-12). Further screening of the reaction condition revealed that the oxidation of benzyl alcohol could be efficiently proceeded in the presence of TEMPO@PMO-IL-Br (1.5 mol%), TBN (10 mol%), AcOH (30 mg), in toluene (0.5 ml) under atmospheric pressure of O$_2$ at 50 °C (Table 1, entries 13, 14). It was also noted that the decreasing of either the TEMPO@PMO-IL-Br loading or reaction temperature resulted in significantly lower yields (Table 1, entries 10, 13). Notably, the use of SBA-15-functionalized TEMPO (TEMPO@SBA-15, 0.33 mmol TEMPO g^{-1}),[4b] TEMPO@PMO-IL-Cl, PMO-IL-AMP, and PMO-IL/TEMPO@SBA-15 was shown to afford considerably lower product yields, demonstrating the critical role of both co-supported TEMPO and ILs in obtaining satisfactory catalytic activity (Table 1, entries 15-18). In all of these cases, the total amounts of the materials were adjusted to keep constant the mol% of functionalized TEMPO and immidazolium units introduced into the individual described reactions. These results clearly highlight that the combination of imidazolium bromide units in the close proximity of TEMPO moieties in the nanospaces of TEMPO@PMO-IL-Br in one of the key factor explaining the enhanced catalytic activity observed for this catalyst in oxidation of benzyl alcohol as compared to that either TEMPO@SBA-15 not bearing IL or individual catalytic functionalities (PMO-IL/ TEMPO@SBA-15).

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Although, the relative loading of imidazolium groups and itsration with TEMPO functions might be important in enhancing the performance of the present catalyst system, our attempts to increase the IL molar ratios in the PMO-IL led to significantly less ordered PMO-IL as evidence by N_2-sorption and TEM analysis.[7c] Moreover, our investigations showed that when a sample of PMO-IL having 25% imidazolium moiety was employed, the resulting TEMPO catalyst system exhibited a lower activity suggesting that an optimal IL loading around 10% (0.98 mmol g^{-1}) and highly ordered mesoporous structure of the materials needs to be respected (Table 1, entry 19). We have also investigated the aerobic oxidation of benzyl alcohol using a mixture of PMO-IL (40 mg) and homogeneous TEMPO (1.5 mol%) to further clarify the crucial importance of co-supported TEMPO and imidazolium bromide in obtaining high catalytic activity in the described catalyst system (Please see Teble 1, entries 18, 20).

Table 1. Optimization of the conditions for aerobic oxidation of benzyl alcohol

Entry	Cat. (mol%)	Solvent (ml)	AcOH (mg)	NO_x (10 mol%)	Yield[a] (%)
1	0.75	Water (2)	-	$NaNO_2$	1.8
2	0.75	Water (2)	20	$NaNO_2$	5.2
3	0.75	Water (1)	20	$NaNO_2$	9
4	0.75	Water (0.3)	20	$NaNO_2$	21
5	0.75	Water (0.3)	20	TBN	27
6	0.75	Toluene (1)	20	$NaNO_2$	5
7	0.75	Toluene (0.5)	20	NaNO2	19
8	0.75	Toluene (1)	-	TBN	3
9	0.75	Toluene (1)	20	TBN	30
10	0.75	Toluene (0.5)	30	TBN	40
11	0.75	Toluene (0.5)	-	TBN	22
12	-	Toluene (0.5)	30	TBN	15
13	**1.5**	**Toluene (0.5)**	**30**	**TBN**	**>99**
14	1.5	Toluene (0.5)	20	TBN	75
15	1.5	Toluene (0.5)	30	TBN	32[b]
16	1.5	Toluene (0.5)	30	TBN	8[c]
17	1.5	Toluene (0.5)	30	TBN	7[d]
18	1.5	Toluene (0.5)	30	TBN	48[e]
19	1.5	Toluene (0.5)	30	TBN	24[f]
20	1.5[g]	Toluene (0.5)	30	TBN	41

[a]The reactions were performed using benzyl alcohol at 50 ºC for 1h. [b]The reaction was performed usingTEMPO@SBA-15 (1.5 mol% TEMPO, 45 mg). [c]The reaction was performed in the presence of PMO-IL-AMP (60 mg). [d]The reaction was performed in the presence of PMO-IL (40 mg) and TEMPO@SBA-15 (1.5 mol% TEMPO, 45 mg). [e]The reaction was performed in the presence of TEMPO@PMO-IL-Cl (60 mg). [f]The reaction was perform in the presence of TEMPO supported on PMO-IL containing 25% IL. [g]The reaction was performed using PMO-IL (40 mg), homogeneous TEMPO (1.5 mol%).

With this optimal reaction conditions, we then investigated the scope of this protocol for other alcohols. As illustrated in Table 2, various types of primary and secondary benzylic alcohol with electron-withdrawing and electron-donating groups were selectively transformed to the corresponding benzaldehydes and ketones in excellent yields under the optimal reaction conditions (Table 2, entries 1–23). Similarly, the TEMPO@PMO-IL-Br catalyst system for aerobic oxidation of primary and secondary aliphatic alcohol to corresponding

aldehydes and ketones showed excellent activity and selectivity (Table 2, entries 24-30).

Table 2. Aerobic Oxidation of Various Alcohols using TEMPO@PMO-IL-Br

Entry	R^1	R^2	Time (h)	Yield[a] (%)
1	C_6H_5	H	1	>99
2	$2,6\text{-}Cl\text{-}C_6H_5$	H	8.5	>99
3	$3\text{-}Cl\text{-}C_6H_5$	H	1	>99
4	$2,4\text{-}Cl\text{-}C_6H_5$	H	1	>99
5	$2\text{-}Cl\text{-}C_6H_5$	H	1	>99
6	$4\text{-}Me\text{-}C_6H_5$	H	1.5	>99
7	$2\text{-}Me\text{-}C_6H_5$	H	3	>99
8	$3\text{-}Me\text{-}C_6H_5$	H	1.5	>99
9	$4\text{-}NO_2\text{-}C_6H_5$	H	1	>99
10	$3\text{-}NO_2\text{-}C_6H_5$	H	1	>99
11	$4\text{-}SMe\text{-}C_6H_5$	H	1	>99
12	1-Naphtyl	H	1.5	>99
13	$4\text{-}OMe\text{-}C_6H_5$	H	1	>99
14	3-Pyridyl	H	1	>99
15	Thiophenyl	H	1	>99
16	Hydroxymethylfurfural		1	>99
17	Furyl	H	1	>99
18	C_6H_5	Me	2	>99
19	$4\text{-}Phenyl\text{-}C_6H_5$	Me	2	>99[b]
20	C_6H_5	Ethyl	2	>99
21	C_6H_5	cyclohexyl	4	>99[b]
22	α-Tetralol		4	>99
23	1-indanol		3	>99
24	$PhCH_2CH_2$	H	3	>99
25	$CH_3(CH_2)_6$	H	4	>99
26	$CH_3(CH_2)_5$	H	4	>99
27	$CH_3(CH_2)_5$	Me	12	80
28	$CH_3(CH_2)_4$	Me	12	80
29	$CH_3(CH_2)_{10}$	H	6	94
30	$CH_3(CH_2)_8$	H	4	96
31	Ph-CH=CH	H	21	22
32	Ph-CH=CH	H	5	95[c]
33	Dicyclopropylcarbinol		5	>99
34	1-Octyn-3-ol		5	93
35	2-Norbornano		9	>99
36	2-Adamantanol		5	94
37	Ph-CH=CH	Ph	6	37
38	Ph-CH=CH	Ph	6	97[d, b]
39	$4\text{-}Me\text{-}C_6H_5\text{-}CH\text{=}CH$	Ph	6	81[d, b]
40	$4\text{-}NO2\text{-}C_6H_6\text{-}CH\text{=}CH$	Ph	6	87[d, b]
41	$2,4\text{-}Cl\text{-}C_6H_6\text{-} CH\text{=}CH$	Ph	6	85[d, b]
42	$3\text{-}OMe\text{-}C_6H_6\text{-} CH\text{=}CH$	Ph	6	94[d, b]

[a]Purity of the products was analyzed by GC. [b]Purity of the product was analyzed by NMR. [c]The reactions were performed using 20 mol% TBN. [d]The reactions were performed using 2 mol% cat., 15 mol% TBN and 10 mg AcOH

Generally, catalytic systems based on transition metal are not always suitable for aerobic oxidation of heteroatom-functionalized alcohols, because these substrates are

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susceptible to coordinate the metal center and deactivate the catalyst. Our catalyst system proved to be efficient for aerobic oxidation of alcohols for bearing common heteroatoms, giving the corresponding aldehydes in excellent yields (Table 2, entries 11 and 14-17). Although we observed a lower activity for highly challenging, sterically hindered alcohols in the presence of TEMPO@PMO-IL-Br, but excellent result could be still retained by increasing the reaction time (Table 2, entries 2, 35 and 36). Notably, the similar transformations are very difficult (or need longer reaction times) to proceed even in AcOH as reaction solvent using previously developed heterogeneous TEMPO/O_2 systems.[4b, 12]

Of particular interest is that 5-hydroxymethylfurfural (5-HMF), a versatile bio-based platform chemical, can be selectively oxidized under the optimized reaction condition (1.5 mol% TEMPO@PMO-IL, 30 mg AcOH, Toluene, 50 °C) to afford 2,5-diformylfuran (DFF), an important platform derived from 5-HMF for the synthesis of the pharmaceuticals, macrocyclic ligands, and others (Scheme 2).[13]
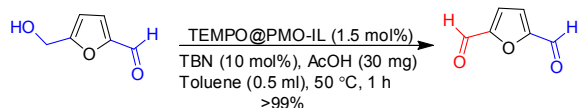
Scheme 2. Aerobic oxidation of 5-HMF into DFF using TEMPO@PMO-IL-Br.

In addition, acid sensitive propargylic alcohols and dicyclopropylcarbinol could be effectively oxidized using the present method and gave excellent yields of the corresponding α,β-unsaturated carbonyl products (Table 2, entries 31-34, 37-42).[11] However, it was found that the oxidation of more sensitive alcohols to acid environment such as cinnamyl and benzylic-allylic alcohols was not successful. In particular, the reaction of (E)-1,3-diphenyl-2-propen-1-ol gave only 37% of the corresponding carbonyl along with 57% yields of the respected symmetrical ether under the optimal conditions (Scheme 3).
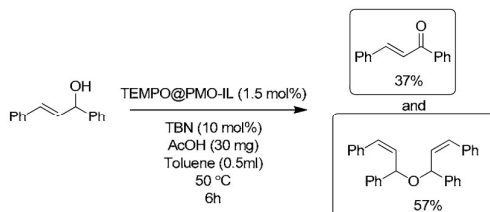
Scheme 3. Symmetrical ether formation in the aerobic oxidation of highly acid sensitive substrate (E)-1,3-diphenyl-2-propen-1-ol at the optimal condition.

Therefore, it was decided to investigate the oxidation of corresponding alcohols in the different conditions. It was found that the use of 20 mol% of TBN and lower amounts of acetic acid (10 mg) and 15 mol% of TBN and 10 mg of acetic acid was better suited for the oxidation of cinnamyl alcohol and (E)-1,3-diphenyl-2-propen-1-ol, respectively (Table 2, enteries 32, 38). Similarly, this modified procol could be equally employed for a set of acid-sensitive allylic acohols, furnishing the corresponding α,β-unsaturated carbonyl compounds with in high selectivity (Table 2, entries 39-42).

The reusability and recovery of the catalyst are important issues, especially when the reactions employ solid catalysts. The recyclability of TEMPO@PMO-IL was also investigated by isolating it from the reaction mixture of aerobic oxidation of benzyl alcohol, washing with EtOAc and acetone and drying (Figure 5). The recycled catalyst was then successfully used in 8 consecutive reaction runs with just slight decrease in activity. The recovered catalyst after 8 run was also studied by N_2-adsorption–desorption analyses. The N_2 sorption diagram of the recovered catalyst TEMPO@PMO-IL interestingly showed a type IV isotherm with relatively sharp hysteresis loop (Figure 1, S11), which indicates that the high-ordered mesostructures have survived. TEM micrograph of the fresh and recovered catalyst after 8 runs demonstrates the high-ordered mesostructure is not destroyed (Figure 3).
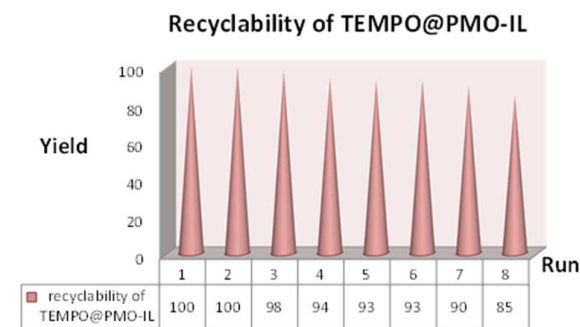

Figure 5. Recyclability of TEMPO@PMO-IL-Br in the aerobic oxidation of benzyl alcohol

On the basis of several successful studies underlying the mechanism for metal-free aerobic oxidation of alcohols using homogeneous TEMPO in the presence of various NO_x sources under homogeneous conditions and our observarion regarding the importance of co-supported TEMPO and imidazolium bromides usits (Table 1, entries 15-20),[3d, 4a, c] a plausible reaction pathway was proposed and in Scheme 4.
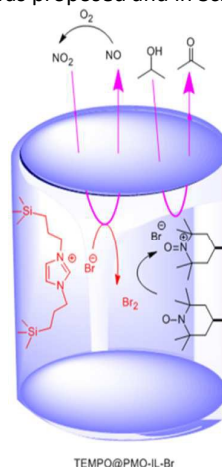
Scheme 4. Proposed reaction pathway highlighting the role of close proximity of imidazolium bromide and TEMPO inside the mesopores of TEMPO@PMO-IL-Br in fast electron transfer from alcohol to molecular oxygen through a synergistic catalysis relay.

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In this proposed pathway, the role of close proximity of of TEMPO moieties with imidazolium bromide units in the mesochannels of PMO-IL in enhancement of electron transfer from alcohol to O_2 by NO/NO_2 couples, immobilized Br^-/Br_2 and immobilized nitroxyl radical through a combination of two successive redox cycles is highlighted.

Conclusion

In summary, we have introduced a bifunctional catalyst compose of TEMPO anchored in the nanospaces of a periodic mesoporous organosilica with imidazolium bromide network. Thanks to the close proximity of TEMPO moieties with imidazolium bromide units in the same solid, while the materials shows enhanced catalytic activity in the metal-free aerobic oxidation of various activated and non-activated alcohols through a synergistic catalysis relay mechanism, the strategy allows simultaneous recovery of both ionic liquid and TEMPO catalyst. This unprecedented cooperative effect results in much superior activity of TEMPO@PMO-IL-Br in oxidation of alcohols as compared to that either TEMPO@SBA-15 not bearing IL or individual catalytic functionalities (PMO-IL/TEMPO@SBA-15)

Experimental Section

Preparation of PMO-IL.[7a] In a typical synthesis, Pluronic P123 (1.67 g) and KCl (8.8 g) were added to a solution of distilled water (10.5 g) and HCl (2 M, 46.14 g) with stirring at 40 °C. After a clear homogeneous solution obtained, a pre-prepared homogeneous mixture of ionic liquid 1,3-bis(trimethoxysilylpropyl) imidazolium chloride (2 mmol, 0.86 g) and tetramethoxysilane (18 mmol, 2.74 g), in super-dry methanol was rapidly added and stirred at the same temperature for 24 h. The temperature of resulting mixture was then raised to 100 °C and the content of flask was statically maintained at this temperature for 72 h. The obtained solid material containing surfactant was filtered, washed with deionized water, and dried at room temperature. The surfactant residue was then extracted from the materials through a Soxhlet apparatus by using ethanol (100 ml) and concentrate HCl (37%, 3 ml) for 24 h.

Preparation of PMO-IL-AMP.[4b] In a typical procedure, 3 g of synthesized PMO-IL was mixed and refluxed with 3-aminopropyltrimethoxysilane (1 mmol, 0.23 mL) in dry toluene for 18 h under argon atmosphere. The white solid materials were filtered and washed with toluene and ethanol in order to remove unreacted 3-aminopropyltrimethoxysilan. The material was then dried in oven at 105 °C to give the PMO-IL-AMP at a loading of 0.35 mmol g-1 as determined by thermogravimetric analysis and confirmed by elemental analysis..

Preparation of TEMPO@PMO-IL-Cl.[4b] Reductive amination has been used for the synthesis of TEMPO@PMO-IL-Cl. In a typical procedure, to a mixture of PMO-IL-AMP (3 g) in super-dry CH_3OH (50 mL), 4-Oxo-TEMPO (1.5 mmol, 0.281 g) was added. $NaBH_3CN$ (2 mmol, 0.125 g) was divided into three portions, the first part was added after 3 h, second part after 24 h and

the third part after 48 h. The reaction mixture was stirred vigorously for 3 days at ambient temperature under argon atmosphere. The final product was separated by filtration and washed three times by water (20 ml), methanol (20 ml), and acetone (20 ml) and dried under vacuum at room temperature to give TEMPO@PMO-IL-Cl. The product stored in a refrigerator under inert atmosphere for the next uses.

Preparation of TEMPO@PMO-IL-Br.[11] In a typical experiment, a suspension of TEMPO@PMO-IL-Cl (2 g) in saturated aqueous solution of NaBr (25 ml) was stirred at ambient temperature for 24 h. The final product was separated by filtration and thoroughly washed with deionized water (6×50 ml) and acetone (25 ml), respectively, to remove the generated NaCl and the excess of NaBr from the surface of the material and dried under vacuum to give TEMPO@PMO-IL-Br. The final product stored in a refrigerator under inert atmosphere.

Typical Catalytic Procedure for Oxidation of Alcohols Using TEMPO@PMO-IL-Br. A mixture of alcohol (1 mmol), TBN (10 mol%), AcOH (30 mg) and catalyst (1.5-2 mol%, 60-80 mg) in toluene (0.5-1 mL) was prepared in a flask and charged with pure oxygen (balloon filled, O_2 1 atmosphere). The resulting mixture was stirred at 50 ºC for the time indicated in Table 2. The progress of the reaction was monitored by GC. After completion of the reaction, the solution was diluted with ethylacetate and the catalyst was separated by centrifuge. The resulting solution was then dried with sodium sulfate and the excess solvent was removed under reduced pressure to give the corresponding carbonyl compounds. The purity of the products was analyzed by GC or NMR without any chromatographic purification.

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