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A heteropolyacid-based ionic liquid immobilized onto Fe_3O_4/SiO_2/Salen/Mn as an environmentally friendly catalyst for synthesis of cyclic carbonate

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Abstract Magnetite-polyoxometalate hybrid nanomaterials, Fe_3O_4/SiO_2/Salen/Mn/IL/HPW (MNPs-HPW), was prepared by grafting of $H_3PW_{12}O_{40}$ on the ionic liquid-functionalized Fe_3O_4 magnetite nanoparticles. This catalyst is a recoverable catalyst for the one-pot synthesis of cyclic carbonate derivatives in high to excellent yield under solvent-free conditions. The MNPs-HPW catalyst was characterized via Fourier transform infrared spectroscopy, X-ray diffraction, thermal gravimetric analysis, transmission electron microscopy, and a vibrating sample magnetometer. Moreover, the catalyst could be easily recovered by magnetic separation and recycled for ten times without significant loss of its catalytic activity.

Keywords Magnetic nanoparticles (MNPs) · Salen · Green Chemistry · Ionic liquid · Heteropolyacid · Cyclic carbonate

Introduction

The preparation and the use of nanoparticles (NPs) in organic synthesis has become a subject of intense investigation. In particular, magnetic nanoparticles (MNPs) offer advantages in clean and sustainable chemistry as they can be non-toxic, readily accessible, and retrievable. Additionally, the activity and selectivity of magnetic nano-catalysts can be manipulated by their surface modification [1]. The use of MNPs as catalysts in chemical synthesis has been extensively studied in recent years as the recovery of expensive catalysts after their use are some of the most noticeable features in the sustainable process development [2–5]. Also, ionic liquids have received considerable interest as eco-friendly solvents, catalysts, and reagents in

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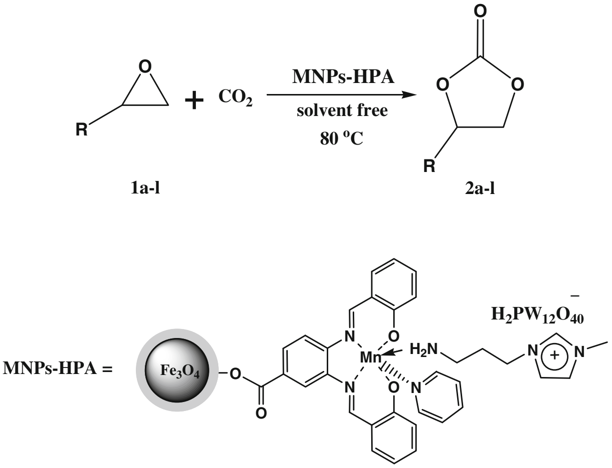
organic synthesis because of their unique properties, such as low volatility, non-flammability, high thermal stability, negligible vapor pressure, and ability to dissolve a wide range of materials [6–8]. Though ILs possessed such promising advantages, their widespread practical application was still hindered by several disadvantages such as high viscosity, which resulted in only a minor part of ILs taking part in the catalyzed reaction for chemical production. There was a homogeneous reaction, which was difficult for separation and reuse procedures; consequently, there was a high cost for the use of relatively large amounts of ILs as opposed to economic criteria [9, 10]. So, in order to reduce these problems, a supported IL catalyst as a novel solid catalyst combining the advantageous characteristics of ILs, inorganic acids, and solid acids had been designed for catalyzed reactions [11, 12]. Heteropolyacids (HPAs) and their salts have been reported as promising heterogeneous catalysts for multi-component reactions [13–18]. Wang Jun's group [19] designed acidic ionic liquid (IL) functional HPAs, and they acted as a "reaction-induced self-separating catalyst" for esterification.

The alarming levels of atmospheric CO_2 consequences increased global warming, which should be dealt at the earliest with utmost attention [20]. An efficient capture from the major CO_2 outlets followed with its proper sequestration could be stated as the only viable technique available so far as a mitigation measure. However, towards a brighter side of utilizing this seemingly non-depletable C1 feedstock, CO_2 could be employed as a possible replacement for the toxic CO and $COCl_2$ for the synthesis of fine chemicals [21–25]. Hence, on grounds of environmental preservation and resource utilization, the chemical fixation of CO_2 into industrially relevant chemical products is receiving ever increased attention. The conversion of CO_2 to cyclic carbonates via epoxide substrates is a 100 % atom economic reaction, and the products are of wide applicability as electrolytes of Li ion batteries, aprotic solvents, degreasing agents, monomers for polymer synthesis, etc. [26–29].

In the past few decades, the numerous heterogeneous and homogeneous catalysts have been developed for the synthesis of cyclic carbonates from epoxides and CO_2 [30–32] - such as metal oxides [33], molecular sieves [34], ion-exchange resins [35], nanoparticles [36], alkali metal salts [37], quaternary ammonium salts [38–40], transition metal complexes [41–44], metal–organic frameworks [45], N-heterocyclic carbenes [46], Lewis acids or bases [47, 48], ionic liquid [49–53], and so on. Among these catalysts, ionic liquids have been shown to have excellent activity in the synthesis of cyclic carbonates from carbon dioxide and epoxides. However, the inherit disadvantage of ionic liquids is the requirement for high CO_2 pressure or transition metal additives [54, 55]. Therefore, the development of a low cost, easily prepared, thermally stable, and efficient single component catalyst for the conversion of CO_2 to cyclic carbonate is still an important task.

In light of the above-mentioned chemistry, the development of new and efficient approaches for the synthesis of these compounds, from simple, readily available starting materials is desirable. We report herein the synthesis of a catalyst, namely tungstophosphoric acid ($H_3PW_{12}O_{40}$)-immobilized IL supported on Fe_3O_4/SiO_2/Salen/Mn for the first time, which catalyzed the synthesis cyclic carbonate from carbon dioxide and epoxides under solvent-free conditions (Scheme 1).



Scheme 1 Synthesis of cyclic carbonate in the presence of MNPs-HPW

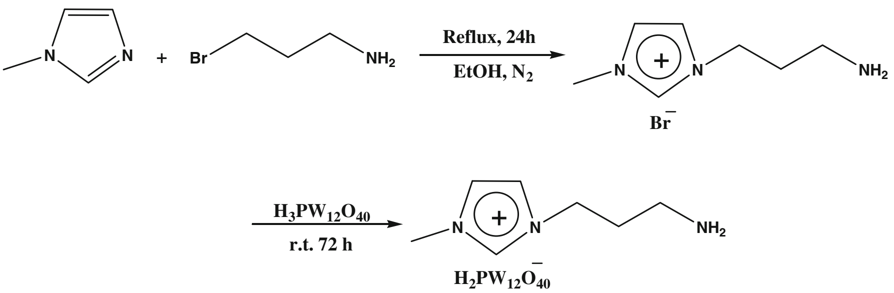
Experimental

Materials and methods

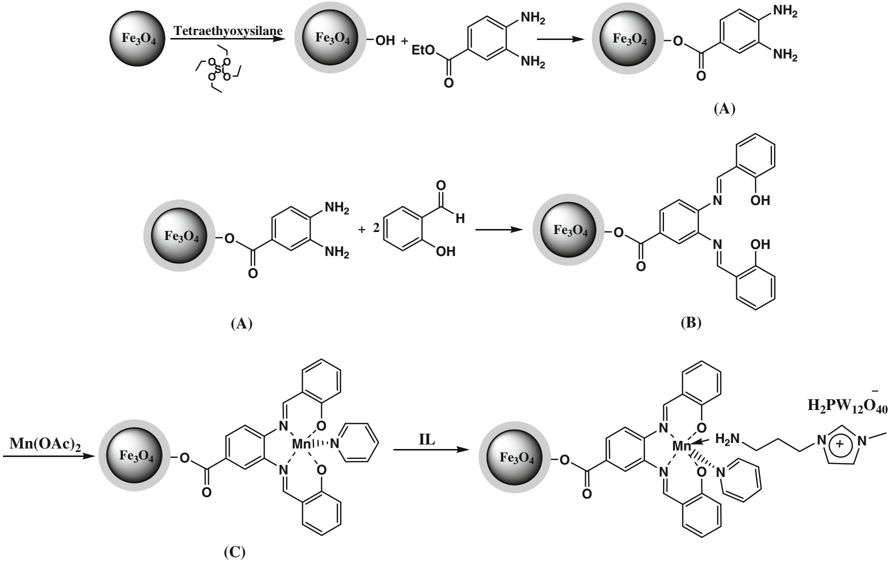
Chemical materials were purchased from Fluka and Merck at high purity. Melting points that were determined in open capillaries using an Electrothermal 9100 apparatus are uncorrected. FTIR spectra were recorded on a VERTEX 70 spectrometer (Bruker) in the transmission mode in spectroscopic grade KBr pellets for all the powders. Morphology was analyzed using high-resolution transmission electron microscopy (HRTEM) on a JEOL transmission electron microscope operating at 200 kV. The content of phosphorous in the catalyst was determined by an OPTIMA 7300DV inductively coupled plasma (ICP) analyzer. Powder X-ray diffraction data was obtained using a Bruker D8 Advance model with Cu ka radiation. The thermogravimetric analysis (TGA) was carried out on a NETZSCH STA449F3 at a heating rate of 10 °C min^{-1} under nitrogen. The magnetic measurement was carried out in a vibrating sample magnetometer (VSM) (4 in., Daghigh Meghnatis Kashan Co., Kashan, Iran) at room temperature. NMR spectra was recorded in $CDCl_3$ on a Bruker Advance DRX-400 MHz instrument spectrometer using TMS as internal standard. The purity determination of the products and reaction monitoring was accomplished by TLC on silica gel polygram SILG/UV 254 plates.

General procedure for the preparation of Fe_3O_4/SiO_2/Salen/Mn/IL/HPW nanoparticles (MNPs-HPW)

Fe_3O_4/SiO_2/Salen/Mn/IL/HPW nanoparticles were prepared by a simple method in our previous work (Schemes 2, 3) [56].



Scheme 2 Synthesis of the IL containing primary amine



Scheme 3 Schematic illustration of the synthesis for MNPs-HPW

General procedures for preparation of cyclic carbonate

MNPs-HPW (0.4 mol%) and epoxide derivatives (1 mmol) were charged into the reactor vessel without using any co-solvent. The reactor vessel was placed under a constant pressure of carbon dioxide and then heated to 80 °C for 2.5 h. Then the reactor was cooled to ambient temperature, and the resulting mixture was transferred to a 50 mL round bottom flask. Upon completion, the progress of the reaction was monitored by TLC, and when the reaction was completed, EtOH was added to the reaction mixture and the MNPs-HPW was separated by an external magnet and washed three times with CH_2Cl_2, ethanol and H_2O. Then the solvent was removed from solution under reduced pressure, and the resulting product purified by recrystallization using *n*-hexane/ethyl acetate.

Data for compounds

Compound (2a) Obtained as a colourless liquid. δ_H ($CDCl_3$) 1.48 (3H, d *J* 6.3 Hz, CH_3), 4.02 (1H, dd *J* 8.3, 7.4 Hz, OCH_2), 4.59 (1H, t *J* 8.3 Hz, OCH_2), 4.84–4.97 (1H, m, OCH); δC ($CDCl_3$) 19.0, 70.2, 73.7, 155.1.

Compound (2b) Obtained as a white solid. Mp 48–50 °C. δ_H ($CDCl_3$) 4.39 (1H, t *J* 8.6 Hz, OCH_2), 4.80 (1H, t *J* 8.4 Hz, OCH_2), 5.68 (1H, t *J* 8.0 Hz, PhCHO), 7.36–7.54 (5H, m, ArH); δ_C ($CDCl_3$) 70.8, 77.6, 125.6, 129.1, 129.9, 137.2, 154.8.

Compound (2c) Obtained as a white solid. Mp 68–71 °C. δ_H ($CDCl_3$) 4.29 (1H, t *J* 7.8 Hz, OCH_2), 4.79 (1H, t *J* 8.4 Hz, OCH_2), 5.70 (1H, t *J* 7.9 Hz, OCH), 7.34 (2H, d *J* 8.5 Hz, ArH), 7.45 (2H, d *J* 8.5 Hz, ArH); δ_C ($CDCl_3$) 70.9, 76.9, 127.4, 130.1, 134.5, 136.1, 154.2.

Compound (2d) Obtained as a white solid. Mp 70–73 °C. δ_H ($CDCl_3$) 4.29 (1H, t *J* 8.2 Hz, OCH_2), 4.83 (1H, t *J* 8.4 Hz, OCH_2), 5.64 (1H, t *J* 8.0 Hz, OCH), 7.23 (2H, dd *J* 8.4, 1.8 Hz, ArH), 7.60 (2H, dd *J* 8.1 Hz, 2.0 Hz, ArH); δ_C ($CDCl_3$) 70.9, 76.9, 124.0, 127.5, 132.1, 134.9, 154.2.

Compound (2e) Obtained as a colourless liquid. δ_H (DMSO-d_6) 3.49 (1H, dd *J* 12.6, 3.2 Hz, CH_2OH), 3.69 (1H, dd *J* 12.6, 2.6 Hz, CH_2OH), 4.30 (1H, dd *J* 8.1, 5.8 Hz, CH_2O), 4.46 (1H, t *J* 8.3 Hz, CH_2O), 4.72–4.89 (1H, m, OCH), 5.29 (1H, br, OH); δ_C (DMSO-d_6) 60.8, 65.7, 77.1, 154.9.

Compound (2f) Obtained as a colourless liquid. δ_H ($CDCl_3$) 3.68–4.02 (2H, m, CH_2Cl), 4.48 (1H, dd *J* 9.0, 8.7 Hz, OCH_2), 4.64 (1H, t *J* 8.5 Hz, OCH_2), 4.92–5.12 (1H, m, OCH); δ_C ($CDCl_3$) 44.1, 67.3, 74.8, 154.6.

Compound (2g) Obtained as a white solid. Mp 96–99 °C. δH ($CDCl_3$) 4.14 (1H, dd *J* 10.6, 3.6 Hz, CH_2OPh), 4.29 (1H, dd *J* 10.6, 4.2 Hz, CH_2OPh), 4.52–4.78 (2H, m, OCH_2), 5.07–5.17 (1H, m, OCH), 6.90–7.09 (2H, m, 2 × ArH), 7.07 (1H, t *J* 7.5 Hz, ArH), 7.20–7.59 (2H, m, 2 × ArH); δ_C ($CDCl_3$) 66.5, 67.7, 73.9, 115.2, 122.4, 130.1, 154.6, 157.9.

Compound (2h) Obtained as a colourless liquid. δ_H ($CDCl_3$) 0.93 (3H, t *J* 7.1 Hz, CH_3), 1.23–1.61 (4H, m, 2 × CH_2), 1.68–2.09 (2H, m, CH_2), 4.10 (1H, dd *J* 8.4, 7.2 Hz, OCH_2), 4.54 (1H, t *J* 8.1 Hz, OCH_2), 4.71 (1H, qd *J* 7.5, 5.4 Hz, OCH); δ_C ($CDCl_3$) 13.3, 21.9, 26.7, 33.2, 69.4, 76.9, 155.1.

Compound (2i) Obtained as a colourless liquid. δ_H ($CDCl_3$) 0.89 (3H, t *J* 6.8 Hz, CH_3), 1.12–1.61 (12H, m, 6 × CH_2), 1.68–1.90 (2H, m, CH_2), 4.07 (1H, dd *J* 8.4, 7.2 Hz, OCH_2), 4.48 (1H, dd *J* 8.4, 7.8 Hz, OCH_2), 4.62–4.82 (1H, m, OCH); δ_C ($CDCl_3$) 14.4, 22.9, 24.3, 29.2, 29.6, 32.1, 34.2, 69.8, 77.3, 155.7.

Compound (2g) Obtained as a white solid. Mp 37–39 °C. δ_H ($CDCl_3$) 2.38 (3H, s, CH_3), 4.29 (1H, t *J* 8.4 Hz, OCH_2), 4.73 (1H, t *J* 8.4 Hz, OCH_2), 5.61 (1H, t *J* 8.1 Hz, OCH), 7.25 (4H, s, ArH); δ_C ($CDCl_3$) 19.8, 70.1, 77.3, 125.1, 128.5, 131.9, 138.3, 153.8.

Compound (2k) Obtained as a white solid. Mp 67–70 °C. δ_H ($CDCl_3$) 2.51 (3H, s, SCH_3), 4.36 (1H, t *J* 9.0 Hz, OCH_2), 4.74 (1H, t *J* 8.7 Hz, OCH_2), 5.60 (1H, t *J* 8.1 Hz, OCH), 7.31 (4H, s, ArH); δ_C ($CDCl_3$) 15.3, 71.5, 78.1, 126.5, 126.7, 132.3, 141.6, 154.8.

Compound (2l) Obtained as a colourless liquid. δ_H ($CDCl_3$) 1.03 (3H, t *J* 7.1 Hz, CH_3), 1.63–2.09 (2H, m, CH_2), 4.10 (1H, dd *J* 6.3, 5.3 Hz, OCH_2), 4.51 (1H, t *J* 8.1 Hz, OCH2), 4.52–4.74 (1H, m, OCH); δ_C ($CDCl_3$) 8.4, 26.8, 69.3, 78.2, 155.8.

Results and discussion

The $Fe_3O_4\backslash SiO_2$ coreeshell was synthesized by a simple method and then functionalized by the Schiff base complex of Mn(III), which had been obtained by the reaction between Mn(III) acetate and the Schiff base prepared from 1,2-benzenediamine and salicylaldehyde, according to Schemes 2 and 3. Then Fe_3O_4/SiO_2/Salen/Mn/IL MNPs was synthesized due to strong coordination between the metal center and the amino group of the IL. The synthesized MNPs-HPW was then characterized by different methods such as X-ray diffraction (XRD), TEM, VSM, FTIR, and TGA. The loading amount of nitrogen was 1.29 mmol per gram solid based on the nitrogen content determination via CHN microanalyses. The loading amount of Mn and HPW were 2.1 and 1.8 wt% as determined by inductively coupled plasma mass spectrometry (ICP-MS). The as synthesized catalyst can be well dispersed in various polar or nonpolar solvents, such as water, ethanol, acetone, DMF, ethyl acetate, cyclohexane, etc.

In order to optimize the reaction conditions and obtain the best catalytic activity, the reaction of propylene oxide (1 mmol), MNPs-HPW (1 mol%) under a constant pressure of carbon dioxide was used as a model, and was conducted under different reaction parameters such as solvent and amount of catalyst. Initially, the model reaction was carried out in several solvents such as EtOH, H_2O, CH_3CN, THF, CH_2Cl_2, EtOAc, DMF, Toluene, *n*-hexane, $CHCl_3$, DMSO, MeOH, dioxane, and under solvent-free conditions, to investigate the efficiency of the catalyst. In this study, it was found that conventional heating under solvent-free conditions is more efficient than using organic solvents, with respect to reaction time and yield of the desired propylene carbonate (Table 1). Then the reaction progress in the presence of MNPs-HPW was monitored by GC (Fig. 1). Using this catalyst system, excellent yields of propylene carbonate can be achieved in the presence of 0.4 mol%. No apparent by-products were observed by GC in all the experiments and the cyclic carbonate was obtained cleanly in 98 % yield.

We also investigated the crucial role of temperature and pressure in the fixation of CO_2 with propylene oxide in the presence of MNPs-HPW as a catalyst. This clearly indicated that the catalytic activity is sensitive to reaction temperature. The best temperature for this reaction was 80 °C. Temperatures >80 °C did not cause changes in the efficiency of the reaction (Fig. 2). Effects of CO_2 pressure in the presence of propylene oxide and MNPs-HPW catalyst at 80 °C for 3 h is shown in

Table 1 Synthesis of propylene carbonate by MNPs-HPW in different solvents

Entry	Solvent	Yield (%)[a]
1	EtOH	72
2	H_2O	81
3	CH_3CN	–
4	THF	38
5	CH_2Cl_2	31
6	EtOAc	42
7	DMF	–
8	Toluene	–
9	*n*-Hexane	–
10	$CHCl_3$	47
11	DMSO	88
12	MeOH	61
13	Dioxane	–
14	Solvent-free	98

Reaction conditions: propylene oxide (1 mmol), MNPs-HPW (1 mol%), and CO_2 1.5 Mpa, under reflux of solvents after 3 h

[a] Isolated yields

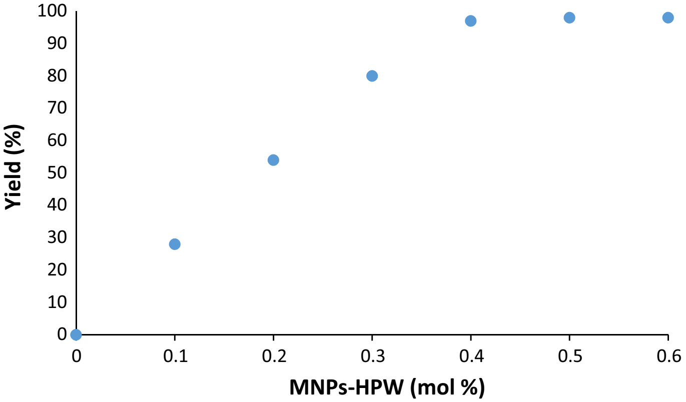


Fig. 1 Effect of the catalyst concentration: propylene oxide (1 mmol), and CO_2 1.5 Mpa in different amounts of MNPs-HPW at 120 °C in 3 h under solvent-free conditions

Fig. 3. The catalyst mixture reaches an average of >98 % of conversion at 1 Mpa pressure.

The effect of time on the present reaction system is shown in Fig. 4. It was found that the reaction time had a remarkable influence on the yield of propylene carbonate. As shown in Fig. 4, the yield of propylene carbonate rose rapidly within the first 2.5 h and remained almost invariably after 2.5 h. So, it was apparent that a reaction time of 2.5 h was appropriate for the synthesis of cyclic carbonate in the presence of MNPs-HPW.

To further evaluate the efficiency of the catalyst, different control experiments were performed and the obtained data is shown in Table 2. Firstly, when Salen/Mn

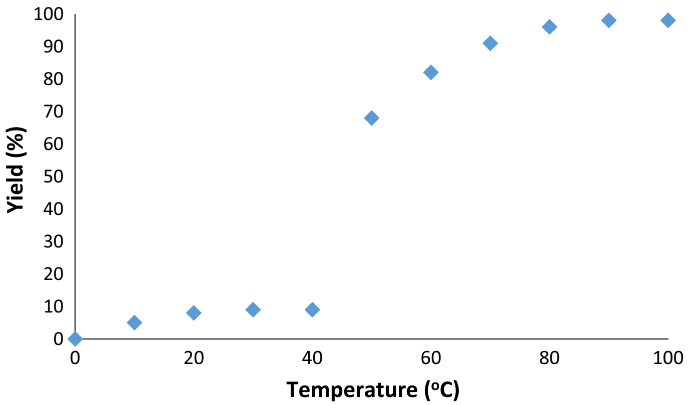


Fig. 2 Effect of temperature on yield of propylene carbonate: propylene oxide (1 mmol), MNPs-HPW (0.4 mol%), CO_2 1.5 Mpa in 3 h under solvent-free conditions

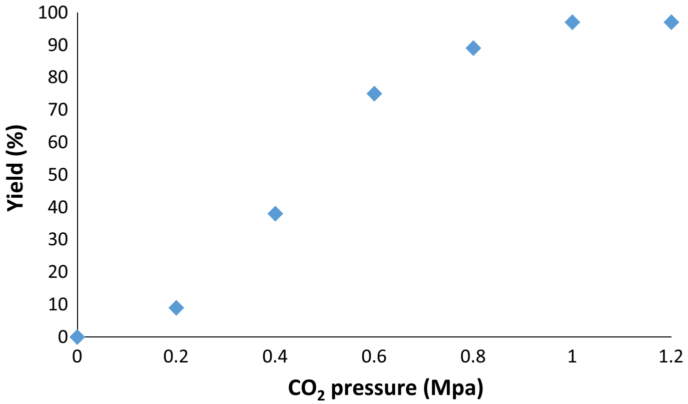


Fig. 3 Effect of pressure on yield of propylene carbonate: propylene oxide (1 mmol), MNPs-HPW (0.4 mol%) at 80 °C in 3 h under solvent-free conditions

or Fe_3O_4/SiO_2 was used as the catalyst, a reaction was still observed, although the yield of the desired product was low (Table 2, entries 1 and 2). Based on these frustrating results, we continued the research to improve the yield of the product by the optimization of the reaction conditions. To our delight, the reaction performed smoothly with the use of Fe_3O_4/SiO_2/Salen/Mn/IL/HPW MNPs and IL/HPW as the catalyst, and the Fe_3O_4/SiO_2/Salen/Mn/IL/HPW MNPs was more effective than IL/HPW (Table 2, entries 3 and 4). As a result, Fe_3O_4/SiO_2/Salen/Mn/IL/HPW MNPs was used in the subsequent investigations because of its high reactivity, high selectivity, and easy separation.

Since MNPs-HPW was the most active of the one-component catalysts, it was tested in the conversion of nine other terminal epoxides (**1a–l**) into the corresponding cyclic carbonates (**2a–l**) (Scheme 1), results being shown in Table 3.

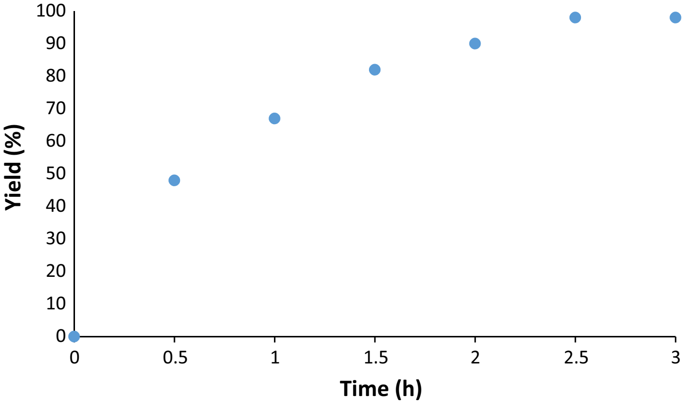


Fig. 4 Effect of time on yield of propylene carbonate: propylene oxide (1 mmol), MNPs-HPW (0.4 mol%), CO_2 1 Mpa at 80 °C under solvent-free conditions

Table 2 Influence of different catalysts on the reaction of epoxide and carbon dioxide

Entry	Catalyst	Yield (%)[a]
1	Fe_3O_4/SiO_2	35
2	Salen/Mn	47
3	IL/HPW	86
4	Fe_3O_4/SiO_2/Salen/Mn/IL/HPW	98

Reaction conditions: propylene oxide (1 mmol), CO_2 1 Mpa, and 0.4 mol% of catalyst at 80 °C in 2.5 h under solvent-free conditions

[a] Isolated yield

Table 3 Synthesis of cyclic carbonate derivatives catalyzed by MNPs-HPW

Entry	R	Product	Yield (%)[a]
1	Me	**2a**	98
2	Ph	**2b**	92
3	4-ClC_6H_4	**2c**	93
4	4-BrC_6H_4	**2d**	92
5	$HOCH_2$	**2e**	87
6	$ClCH_2$	**2f**	95
7	$PhOCH_2$	**2g**	87
8	Bu^n	**2h**	93
9	Oct^n	**2i**	91
10	4-MeC_6H_4	**2j**	90
11	4-$MeSC_6H_4$	**2k**	89
12	Et	**2l**	93

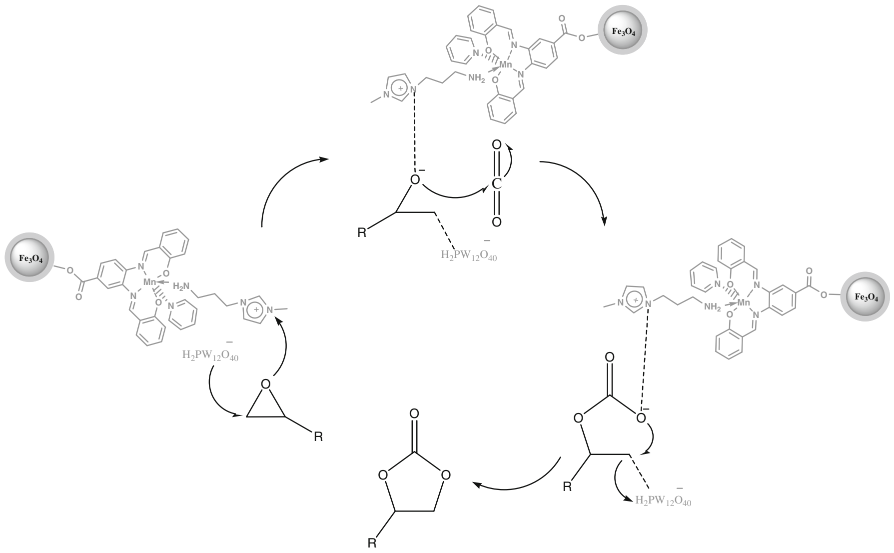
Reaction condition: epoxide derivatives (1 mmol), MNPs-HPW (0.4 mol%), CO_2 1 Mpa at 80 °C in 2.5 h under solvent-free conditions

[a] Yield refers to isolated product

In each case, the cyclic carbonate was obtained with good to excellent isolated yield after 2.5 h using 0.4 mol% of catalyst under solvent-free conditions at 80 °C under a constant pressure of carbon dioxide.

The exact mechanism of the reaction is not known at this stage; however, based on the known mechanism, the possible mechanism of the reaction involves the epoxide ring opening by the nucleophilic attack of $H_2PW_{12}O_{40}^-$ ion. The promoting effect of imidazolium is due to its non-bonding interaction with the oxygen of epoxide, which may facilitate the ring opening of the oxirane ring. The ring opening, leads to the formation of oxy anion species, which on subsequent reaction with carbon dioxide and subsequent cyclization, may give the corresponding carbonate (Scheme 4).

To verify whether or not the catalysis is truly heterogeneous or is due to some leached active species present in the liquid phase, the model reaction of propylene oxide and carbon dioxide was carried out under the optimized conditions, and the catalyst was separated by applying an external magnetic field from the reaction mixture. Inductively coupled plasma mass spectrometry (ICP-MS) analysis showed that the amount of Mn and HPW leaching into the reaction mixture is very low (0.2 ppm). These observations indicated that the catalyst was stable and could tolerate the present reaction conditions. The recyclability of catalyst was examined using the model reaction under identical conditions. After the required time, the catalyst was recovered from the reaction mixture by magnetic separation, washed with ethyl acetate, and subsequently dried at 100 °C, then reused. After ten consecutive reuses, the catalyst exhibited almost identical catalytic activity (Fig. 5). Furthermore, the TEM images of the catalyst after ten recycles did not show



Scheme 4 Catalytic cycle for cyclic carbonate synthesis

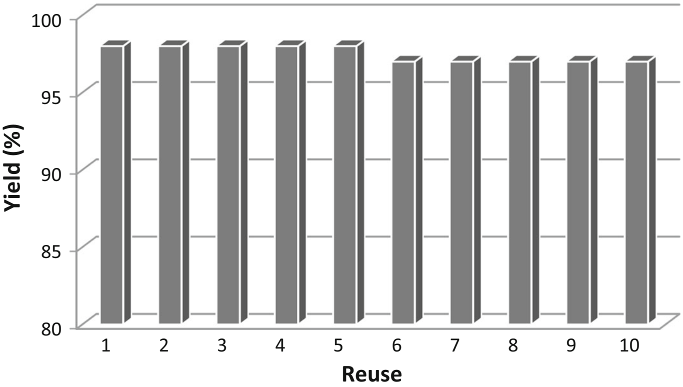


Fig. 5 Reuse performance of the catalysts. Reaction conditions: propylene oxide (1 mmol), MNPs-HPW (0.4 mol%), CO_2 1 Mpa at 80 °C in 2.5 h under solvent-free conditions

noticeable change in the shape and size of catalyst particles compared to fresh MNPs-HPW.

Conclusion

In conclusion, we have developed a heterogeneous catalyst based on the concept of supported IL phase catalysis. The amounts of both ionic liquids as well as the transition metal species involved in the preparation of catalysts were low and the preparation procedure was easy, thus displaying very good performance from an economic point of view. The catalyst was well characterized by different physicochemical techniques to confirm its structural integrity. The synthesized Fe_3O_4/SiO_2/Salen/Mn/IL/HPW MNPs was used as a magnetically recyclable heterogeneous catalyst for the efficient one-pot synthesis of cyclic carbonates with high product yields. This catalyst offers notable advantages such as a heterogeneous nature, easy separation by an external magnetic field, good to excellent product yields, easy preparation, short reaction times, and simplicity of handling. In addition, the catalyst used is easily recovered by using an external permanent magnet and reused ten times without any noticeable loss of activity .

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