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Palladium-salen-bridged ionic networks immobilized on magnetic dendritic silica fibers for the synthesis of cyclic carbonates by oxidative carboxylation

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Compared to epoxides, converting carbon dioxide (CO₂) to cyclic carbonates is proposed as the most appropriate way to synthesize C1 building blocks. In this study, a Pd(II) Schiff base complex is fixed on FeNi₃/DFNS nanoparticles and then reacted with melamine to provide a recoverable magnetic heterogeneous nanocomposite of FeNi₃/DFNS/salen/Pd(II). It was determined that the FeNi₃/DFNS nanoparticles are an appropriate catalyst for the oxidation carboxylation of styrenes with CO₂ in a one-step reaction. The FeNi₃/DFNS nanoparticles were characterized *via* XPS, FTIR, EDX, FE-SEM, XRD, TGA, TEM, IC, VSM and BET analyses. The important benefits of this catalyst are its easy work-up, low cost and high efficiency.

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1. Introduction

Converting CO_2 to appropriate organic chemicals is currently an important research area.^{1–5} CO_2 is not only a waste material of chemical industries and greenhouse gas emission, but also a readily available, non-toxic, and non-flammable carbon raw material.^{6,7} Nevertheless, due to the low reactivity of CO_2 , it is not widely utilized in industry. Highly active catalysts, energy inputs, optimization conditions, *etc.*, are key factors in the thermodynamic conversion of stable CO_2 molecules.⁸

Cyclic carbonates are widely utilized in industry as electrolytes in monomers, lithium batteries, intermediate organic synthesis, and aprotic polar solvents. Recently, different cyclic carbonate combination from CO_2 have been synthesized. Among them, the CO_2 cycloaddition to epoxides is one of the common and industrial approaches.^{9,10} Due to the readily available and low cost raw materials, *viz.*, alkenes and no need for epoxide separation after the first step, the direct production of cyclic carbonates from CO_2 and olefins by oxidative carboxylation, as seen in Scheme 1, which includes a mixture of cycloaddition of CO_2 and alkene epoxidation to synthesize epoxides, may be a cost-effective approach.¹¹⁻¹⁸ Olefin oxidative carboxylation was introduced in 1962. However, more investigations on CO_2 cycloaddition to the epoxide ring are still required.¹⁹⁻²¹

Currently, the use of surfactants as soft templates facilities the synthesis of mesoporous silica with a dendrimeric morphology of silica fibers. In terms of adsorption and catalysis, silicas with this specific morphology have been exanimated as support materials. Furthermore, to access functional materials, the apparent development of these silicas yield a high surface area due the reactants used. In addition, dendritic fibrous nanosilica (DFNS) which possesses intrinsic mesoporous characteristics, are thermally stable and have high activity. The synthesis of DFNS involves a microemulsion approach utilizing water, surfactants, and oils. Furthermore, the morphology of DFNS and their particle size may be manipulated using various co-solvents and co-surfactants.^{22–25}

Recently, organometallic ionic complexes (OICs) have been introduced as appreciable catalysts since they are synthesized



Scheme 1 Synthesis of cyclic carbonates through oxidative carboxylation of alkenes.



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Paper

water several times.

2.3. General procedure for the preparation of FeNi₃/SiO₂ **MNPs**

An aqueous solution containing ethanol (80 mL), 2.0 mL of 28 wt.% concentrated ammonia aqueous solution (NH₃·H₂O), and deionized water (20 mL) was produced. In the above mixture, FeNi₃ MNPs (0.02 mol) were dispersed and 0.20 g of tetraethyl orthosilicate (TEOS) was subsequently added. The compound was vigorously stirred for 1 day. The obtaining solid phase was filtered and then washed several times. Subsequently, it was dried at a temperature of 60 °C.

2.4. General procedure for the preparation of FeNi₃/DFNS **MNPs**

Solution A was obtained by adding 30 mL aqueous solution containing a dispersion of 0.25 g of FeNi₃/SiO₂ and 0.3 g urea. Then it was placed in an ultrasonic bath for 60 min. Solution B was obtained adding a 0.5 g cetylpyridinium bromide (CPB) to 0.75 mL of n-pentanol and 30 mL of cyclohexane. Then solutions A and B were mixed and stirred at a temperature of 25 °C, and subsequently 1.25 g TEOS was added dropwise. The mixture was continuously stirred for one hour at temperature of 25 °C. After that, it was placed in an oven at a temperature of 120 °C for 5 h to initiate the reaction. The reaction was cooled to a temperature of 25 °C and strong magnetic suction was used to separate the core-shell microspheres of FeNi3/DFNS. Subsequently, the solid phase was rinsed several times with acetone and water. Finally, the rinsed solid was dried overnight in an oven at 40 °C, and calcined at a temperature of 550 °C for 5 h.

2.5. General procedure for the preparation of FeNi₃/DFNS/ 3-chloropropylsilane MNPs

2 mmol of FeNi₃/DFNS MNPs was added to 20 mL of THF and ultrasonicated with 20 mmol of NaH. 22 mmol of 3-chloropropyltriethoxysilane was added dropwise at a temperature of 25 °C and then the mixture was stirred at a temperature of 60 °C for 16 h. The resultant products were rinsed several times with deionized water and ethanol, and after that dried in a vacuum oven for 2 h at a temperature of 60 °C.

2.6. General procedure for the preparation of Pd(II) Schiff base complex

10.0 mmol of imidazole was added to 2.0 mmol of 2-hydroxy-5chloromethyl benzaldehyde (1) solution in 20 mL of propylene carbonate. Subsequently, the mixture was stirred at a temperature of 90 $^{\circ}C$ under an N₂ atmosphere for 2 days. Then the reaction was cooled to 25 °C, and then a constant amount of water (10 mL) was added. Subsequently, the product was extracted with ethyl acetate (15 mL). The solvent was removed under reduced pressure to yield the desired product 2, and then it was rinsed with dilute deionized water and NaOH and after that dried at a temperature of 50 °C (in an oven). (3) 1.0 mmol of

using highly adaptable and readily available metals.^{26,27} In addition, for multifunctional integration, they are promising ligands. In many studies, for the coupling reaction of CO₂ and other organic combinations via co-catalyst free states, the catalytic functional groups have a significant influence, and OICs which comprise a nucleophilic portion of a halogen anion (X⁻) and a Lewis acid metallic center, function as very impressive bifunctional catalysts.²⁸⁻³⁰ Herein, a novel approach for the production of heterocyclic compounds is proposed via the initiation of the Lewis acid active sites on a halogen anion (X⁻)-based ionic polymers to provide recyclable and highly active catalysts. Subsequently, silica groups are suggested instead of organic groups. For the coupling reactions, we determined that half-salen Pd(II) complexes have catalytically behavior.^{31–40} For catalyst reuse, many heterogenized systems such as magnetic and silica nanoparticles are coupled to salen Pd(II) complexes supported on certain supports. Nevertheless, most catalytic systems exhibit unsatisfactory catalytic performances under harsh reaction conditions.41-45

Herein, FeNi₃/DFNS core-shell NPs were efficiently functionalized with a melamine-Pd(II) Schiff base complex as a new recoverable magnetic heterogeneous nanocatalyst for the efficient, selective, and environmentally friendly production of cyclic carbonates from CO₂ and olefins (refer to Scheme 1).

2. Experimental

2.1. Materials and methods

High purity chemicals were procured from Fluka and Merck. An electrothermal 9100 apparatus was utilized for the determination of uncorrected melting points in open capillaries. A VERTEC 70 spectrometer (Bruker) in transmission mode was used to measure FTIR spectra. Samples were pulverized and pelletized with spectroscopic-grade KBr. Determination of the size and structure of the nanoparticles was performed via transmission electron microscopy (TEM) (Phillips CM10) operated at 100 kV. The crystallographic structures of the nanoparticles were determined using powder X-ray diffraction (Bruker D8 Advance model) with Cu Ka radiation. Thermal gravimetric analysis (TGA) (NETZSCH STA449F3) was performed under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹. Thin layer chromatography (TLC) on silica gel polygramSILG/UV 254 plates was used for the determination of product purity and monitoring of the reaction. A Shimadzu GCMS-QP5050 mass spectrometer was used to record mass spectra.

2.2. General procedure for the preparation of FeNi₃ MNPs

Initially, 0.03 mol NiCl₂·6H₂O and 0.01 mol FeCl₂·4H₂O was dissolved in 300 mL of distilled water. Subsequently, 1.0 g of polyethylene glycol was added (PEG, M_w 6000). NaOH was added to the solution to obtain a specific pH range ($12 \le pH \le 13$). N₂H₄·H₂O, at 80% concentration, was added to the suspension in different quantities. To continue the reaction, the suspension was maintained at a temperature of 25 °C for 24 h. The pH of the suspension was kept constant in the upper mentioned pH range

NJC

4-((1*H*-imidazol-1-yl)methyl)-2-((allylimino)methyl) phenol and Pd ions were dissolved in ethanol (15 mL) and 0.5 mmol of Pd(OAc)₂ was further added. The resulting mixture was stirred at a temperature of 25 °C under an N₂ atmosphere for half a day. Then product 4 was filtered, rinsed with cooled diethyl ether and ethanol, and dried at a temperature of 25 °C.

2.7. General procedure for the preparation of FeNi₃/DFNS/ salen/Pd(II) MNPs

FeNi₃/DFNS-Cl (1 g) was added at a temperature of 90 °C (under an N₂ atmosphere) to a stirred solution of 1.0 mmol Pd(π)–Im-Schiff base complex in a propylene carbonate (20 mL). The mixture was cooled to 25 °C for one day, and then the product was separated using an external magnetic field and then rinsed with propylene carbonate and EtOH to remove any unreacted substrates. Subsequently, it was dried at a temperature of 70 °C for 6 h. The immobilized Pd(π)–Im-Schiff base complex (8) was added to 0.5 mmol of melamine in a dried round-bottom flask and then refluxed with 4.0 mmol of trimethylamine solution in 5.0 mL of absolute MeOH and 4.0 mmol of AlCl₃·2H₂O under an N₂ atmosphere for 6 h.

2.8. Catalytic reactions

The reaction was performed in a stainless-steel autoclave (25 mL). 8 mg of FeNi₃/DFNS/salen/Pd(II), 10 mmol of olefin and 20 mmol of *tert*-butyl hydroperoxide (TBHP) were added to the stainlesssteel autoclave. The mixture was stirred using a magnetic stirrer and then, in a water bath, heated to the desired temperature. The reactor was purged with carbon dioxide several times and then charged with carbon dioxide. Then, the stainless-steel autoclave was heated to the appropriate temperature and stirred for 10 h. The reactor was cooled to 25 °C after the reaction was performed, and the residual CO₂ was discharged slowly from the reactor. The reaction solution was examined using GC-MS and GC.

3. Results and discussion

The results from the elemental investigation of the obtained product is presented in Table 1. The results are consistent with the theoretical calculations and verified the production of a mixture of 1, 2, 3, and 4. In addition, the results confirmed the suggested structure indicated in Scheme 2 and the former structure stated in ref. 46.

The morphology of the synthesized FeNi₃/DFNS/salen/Pd(II) MNPs and FeNi₃/DFNS was analyzed using FE-SEM and TEM. As seen in Fig. 1a, silica fibers, nonporous silica layer, and a core of FeNi₃ particle existed. Fig. 1a and c show the TEM and



Scheme 2 Schematic illustration of the preparation of the FeNi₃/DFNS/ salen/Pd(II) NPs.

FE-SEM images, respectively. As observed, the FeNi₃/DFNS samples have a wrinkled radial structure and also solid spheres with a diameter of 300 nm. Upon close investigation of these images, wrinkled fibers (8.5 nm) can be seen. These fibers are grown from the center of the spheres and radially regulated. In addition, the overlap of the wrinkled radial structure creates conical pores. Furthermore, this hierarchical open channel structure and fibers cause the mass transfer of reactants to be easier and increase the access to the active sites. From the TEM and FE-SEM images of FeNi₃/DFNS/salen/Pd(II) MNPs, it is clear that after modification, the FeNi3/DFNS morphology did not change (refer to Fig. 1b and d). Fig. 2a shows the obtained TGA curve for the Pd-Schiff base complex 4. As can be observed, in the temperature range from 95 °C to 400 °C, there is a one-step decomposition pattern. This weight loss is attributed to the decomposition of the Pd-Schiff base ligand to CO2, cobalt oxides, and CO species due to the thermal decomposition of the oxygenated carbon surface groups (refer to Fig. 2b). The influence of the incorporation of melamine on 6 for the thermal treatment of the FeNi3/DFNS/Im[Cl]Pd(II)-melamine nanocomposite can be easily observed. As shown in Fig. 2c, catalyst 6 exhibited greater thermal stability compared to 5. The thermal analysis of the catalyst indicated 44% weight loss, comprising the decomposition of organic moieties and water. In the temperature range of 95–250 °C, the weight loss of 2.5% is ascribed to the loss of hydrogen-bonded water molecules available on the FeNi₃ core-shell surface. In the temperature range of 300-500 °C, the weight loss of 3.0% is attributed to the removal of H₂O trapped from the lattice. In the temperature

Table 1 Results of the elemental analysis and physical properties of the compounds

	Elemental analysis		
Compound	%Н	%C	%N
2-Hydroxy-5-chloromethyl benzaldehyde (1) 2-Hydroxy-5-imidazole benzaldehyde (2) 4-((1 <i>H</i> -Imidazol-1-yl)methyl)-2-((allylimino)methyl)phenol (3) Pd(n) Schiff base complex (4)	4.14 (4.25) 5.09 (4.98) 6.22 (6.27) 5.02 (5.23)	56.30 (56.82) 65.74 (65.34) 69.47 (69.69) 64.80 (64.34)	 13.97 (13.85) 17.64 (17.41) 15.32 (15.58)



Fig. 1 TEM images of (a) FeNi₃/DFNS MNPs, (b) FeNi₃/DFNS/salen/Pd(\mathfrak{n}) MNPs, (c) FE-SEM images of FeNi₃/DFNS MNPs, and (d) FeNi₃/DFNS/salen/Pd(\mathfrak{n}) MNPs.



Fig. 2 TGA curves of (a) Pd(μ) Schiff base complex **4**, (b) FeNi₃/DFNS/Pd(μ) Schiff base complex (**5**), and (c) catalyst **6**.

range of 500–600 $^{\circ}$ C, the weight loss (38%) is related to the decomposition of the organic moieties on the surface of the FeNi₃/DFNS core–shell nanoparticles.

XPS was performed to investigate the chemical composition on the surface of the FeNi₃/DFNS/salen/Pd(II) MNPs. Fig. 3 shows the XPS spectrum of the as-synthesized catalyst. The peaks of Pd, O, C, N, Si, Fe, Cl, and Ni and the presence of N 1s additionally confirm that DFNS were functionalized by imidazolium. In addition, the presence of Cl⁻ ions (the imidazolium counter ion) was confirmed by the sharp peak at 287 eV, which shows the imidazolium moiety is available within the catalyst. In addition, the XPS scheme of Pd 3d exhibits a doublet, which is indicative of metallic palladium. As seen in Fig. 4, the composition of the catalyst was investigated *via* EDX analysis, which shows the elements that present in the MNPs of FeNi₃/DFNS/salen/Pd(II) including silicon, nickel, carbon, nitrogen, palladium, iron, and oxygen.

The powder X-ray diffraction patterns of the FeNi₃/DFNS/ salen/Pd(π) MNPs and FeNi₃, FeNi₃/DFNS are shown in Fig. 5. As observed in Fig. 5a, for the FeNi₃ sample (JCPDS No. 19-0629),



Fig. 3 XPS spectrum of FeNi₃/DFNS/salen/Pd(II) MNPs.



the common diffraction peaks corresponding to the (220), (200), and (111) planes in all the samples are consistent with the typical XRD data. Besides the peak of iron oxide, the XRD pattern of the FeNi₃/DFNS nanoparticles exhibit a wide peak (at low diffraction angle), related to amorphous silica (refer to Fig. 5b). Fig. 5c shows the XRD pattern of the FeNi₃/DFNS/salen/Pd(π) MNPs, which has no changes.

Additionally, the magnetic characteristics of the samples were studied (refer to Fig. 6). The nanoparticles were magnetized sufficiently to be separated by an external magnetic field. The magnetization curves observed are stable and no hysteresis is observed. The residual magnetization for all the nanoparticles is zero. The saturation magnetization (M_s) values of 25.4 and 59.6 emu g⁻¹ were determined for FeNi₃/DFNS/salen/Pd(II) and FeNi₃ nanocomposite (6), respectively. Fig. 6a and b indicate that the magnetization of FeNi₃ is reduced significantly due to the coating by the silica-shell or Pd(II)-Schiff base complex on its surface. The FeNi₃/DFNS/salen/Pd(II) nanocomposite showed superparamagnetic properties with high magnetization values, which means it can be simply separated from a mixture using a magnetic field.





Fig. 6 Room-temperature magnetization curves of (a) FeNi_3/DFNS, and (b) FeNi_3/DFNS/salen/Pd(μ) MNPs.

To characterize the porosity and specific surface area of the products, N_2 adsorption–desorption isotherm analysis was performed. In accordance with the BJH approach, the mean pore diameter, the total pore volume and the specific surface area values are presented in Table 2. The BET results indicate that the active surface area of the FeNi₃/DFNS/salen/Pd(II) nanocomposite (catalyst (6)), FeNi₃/DFNS, and FeNi₃/DFNS/salen/Pd(II) complex (5) are 386, 688, and 398 m² g⁻¹, respectively. Thus, the results indicate that after melamine intercalation, the specific surface area was reduced. Moreover, the average pore radius and pore volume were enhanced by adding melamine. Thus, melamine intercalation offers a more porous network structure.

In this system, the reaction conditions were optimized using carbon dioxide and olefin for the synthesis of cyclic carbonates catalyzed by $FeNi_3/DFNS/salen/Pd(II)$ nanoparticles. Table 3 shows the effects of various factors such as time and solvent on the model reaction. Different solvents were used to investigate the effect of the solvent on the production of cyclic carbonates. The results showed that no product was synthesized using polar protic solvents such as methanol, isopropanol, water, and ethanol. Polar protic solvents such as DMF, DMSO, and EtOAc showed moderate efficiency in the

Table 2 Structural parameters of FeNi₃/DFNS, FeNi₃/DFNS/salen/Pd(μ) complex (5), and FeNi₃/DFNS/salen/Pd(μ) complex (6) MNPs

Catalysts	S_{BET} $(\text{m}^2 \text{g}^{-1})$		D _{BJH} (nm)
FeNi ₃ /DFNS	688	3.5	9
FeNi ₃ /DFNS/Im[Cl]Pd(II)	398	1.9	4
FeNi ₃ /DFNS/Im[Cl]Pd(II)–melamine	386	2.1	4

Table 3 Synthesis of cyclic carbonate by $\text{FeNi}_3/\text{DFNS/salen/Pd}(\texttt{i})$ MNPs in different solvents a

Entry	Solvent	Time (h)	Yield $(\%)^b$
1	H_2O	20	_
2	i-PrOH	20	_
3	EtOH	20	—
4	MeOH	20	_
5	<i>n</i> -Hexane	20	—
6	Dioxane	20	—
7	DMF	20	27
8	THF	20	32
9	$CHCl_3$	20	29
10	CH_2Cl_2	20	35
11	DMSO	20	30
12	CH ₃ CN	20	26
13	EtOAc	20	41
14	Toluene	20	43
15	Anisole	20	45
16	Solvent-free	20	98
17	Solvent-free	15	98
18	Solvent-free	10	98
19	Solvent-free	5	71

^{*a*} Reaction conditions: appropriate CO₂ (3.0 MPa), olefin (10 mmol), FeNi₃/DFNS/salen/Pd(II) MNPs (10 mg), TBHP (20 mmol), and solvent (10 mL), under reflux or 100 °C. ^{*b*} Isolated yields.

cross-coupling reactions. In this work, the results showed that solvents were less efficient than conventional heating under solvent-free conditions. The cross-coupling reaction efficiency of carbonylation was higher in less polar solvents such as anisole and/or toluene. To investigate the reaction time, the reaction was performed under the optimum conditions in the presence of FeNi₃/DFNS/salen/Pd(II) nanoparticles (10 mg) and the reaction progress was analyzed using GC. It was found that excellent product yields were obtained within 10 h.

The effects of different parameters for the model reaction were investigated using the FeNi₃/DFNS/salen/Pd(II) MNPs. Fig. 7 shows the effect of catalyst amount on the effective yield. Besides, low yields of the product of the cycloaddition reaction were obtained in the absence of the catalyst. Using weighted quantities of FeNi₃/DFNS/salen/Pd(II) nanoparticles (2–6 mg), the cyclic carbonate products showed moderate yields. The optimum amount of FeNi₃/DFNS/salen/Pd(II) nanoparticles for the model reaction was found to be 8 mg.

Fig. 8 shows the effect of temperature on the reaction. As can be seen, the production of cyclic carbonate increased to about 98% at 80 $^{\circ}$ C under 3.0 MPa CO₂ pressure over 10 h. However, a further increase in temperature resulted in a slight decrease in the yield of the product due to a negligible amount of specific byproducts such as olefin isomerization. Therefore, the optimum temperature for the parallel reactions of olefin and carbon dioxide



Fig. 7 Effect of amount FeNi₃/DFNS/salen/Pd(II) MNPs on the yield of cyclic carbonate



Fia. 8

was about 80 °C. The CO₂ pressure had a significant effect on the parallel reaction. As can be seen in Fig. 9, the reaction rate increased rapidly at pressures between 1.5 and 2.0 MPa. From previous studies, it can be concluded that increasing the reaction pressure until the pressure reaches 2.0 MPa is favorable for the production of cyclic carbonate. Therefore, the CO₂ pressure of 2.0 MPa was identified as the optimal condition. Initially, the following conditions were applied for the reaction: 80 °C for a few hours (10 mol%). Different oxidants were used to increase the yield of the product. The reaction yield was extremely sensitive to the base. Specifically, catalyst basicity is not the only parameter in determining activity. According to the results obtained in Fig. 10, the highest yield was obtained using TBHP as an oxidant.



Fig. 9 Effect of CO₂ pressure on the synthesis of cyclic carbonate.





For further investigation of the efficiency of the catalyst, different control experiments were performed, and the obtained results are shown in Table 4. Initially, a standard reaction was carried out using FeNi3 MNPs, which showed that the desired product was not formed after 10 h of reaction time (Table 4, entry 1). In addition, when the FeNi3/DFNS/salen MNPs were used as the catalyst, a reaction was not observed (Table 4, entry 2). Under mild reactions, the catalytic activity of salen was not satisfactory. Since these results were unsatisfactory, further investigation was performed to enhance the yield of the product with the addition of $Pd(\pi)$. Interestingly, a different outcome was obtained in terms of the reaction yield when it was carried out using FeNi3/DFNS/salen/ $Pd(\pi)$ MNPs and salen/ $Pd(\pi)$ catalyst (Table 4, entries 3 and 4). These results indicate that Pd(n) in this catalyst will maximize the catalyst performance. However, salen/Pd(II) could not be used or recovered for the next runs. Based on these observations, it can be concluded that Pd(II) species complexed on the FeNi₃/DFNS/salen/Pd(II) nanostructure catalyze the reaction cycle.

Different olefins were investigated for the study of the substrate scope in this new one-pot process for the synthesis of cyclic carbonates (Table 5). The catalyst was active for all the substrates in Table 5. Besides, aryl olefins bearing a para-chloro group were excellent substrates, which offered near-quantitative products. Aryl olefins, together with the meta or ortho-chloro groups, were also excellent substrates. However, an electrondonating group such as methyl on the aryl group decreased the yield of the product.

Fig. 11 shows that the catalyst can be reused after 10 runs. The yield of cyclic carbonate obtained in the 10th run was 94%,

Table 4 Influence of different catalysts on the cycloaddition of CO₂ with terminal olefins^a

Entry	Catalyst	Yield ^b (%)
1	FeNi ₃	
2	FeNi ₃ /DFNS/salen	_
3	FeNi ₃ /DFNS/salen/Pd(II) [Complex (6)]	98
4	Salen/Pd(II) [Complex (4)]	98

^a Reaction conditions: appropriate CO₂ (2.0 MPa), aniline (1.0 mmol), catalyst (8 mg), and TBHP (20 mmol), under 80 °C. ^b Isolated yield.

Paper

Table 5 Cycloaddition of CO₂ with terminal olefins^a



 a Reaction conditions: appropriate CO $_2$ (2.0 MPa), aniline (1.0 mmol), catalyst (8 mg), and TBHP (20 mmol), under 80 $^\circ \rm C.$

which was only 4% lower compared to the fresh catalyst (98%). In addition, the amount of leached metal in solution for the synthesis of cyclic carbonate after each run was investigated using ICP. As shown in Fig. 12, it was found that very little catalyst was leached in each cycle, and after 10 runs only 0.6% of the metal was leached.

We also performed a complete study to confirm the heterogeneous nature of the catalyst. Initially, a hot filtration experiment for the production of cyclic carbonate was performed under the optimized conditions, which indicated that approximately 71% catalyst was removed magnetically *in situ* (for around 5 h for removal). In







Fig. 12 Recyclability of the catalyst for the synthesis of cyclic carbonate.

addition, the reactants are permissible to tolerate more reaction. After removing the heterogeneous catalyst, the results specified that the free catalyst remnant was fairly active, and the conversion of 74% was obtained after 10 h for the production of cyclic carbonate. This demonstrated that the catalyst acted heterogeneously during the reaction and only slight leaching occurred during the reaction. Subsequently, a mercury poisoning test was additionally performed



Fig. 13 Reaction kinetics, Hg(0) poisoning, and hot filtration studies for the synthesis of cyclic carbonate.

to ensure the heterogeneous nature of the catalyst. Mercury(0) was imbibed as a metal (*via* synthesis). Consequently, it deactivated the metal catalyst on active surface dramatically, and thus deactivated the catalyst. Thus, this experiment demonstrates the heterogeneous nature of the catalyst, which was performed using the model reaction under the optimal conditions. Specifically. around 300 mol mercury was added to the reaction mixture after 5 h of the reaction. The reaction mixture was stirred and after 10 h, due to the catalyst being poisoned, no more conversion was observed. Fig. 13 shows the kinetics of the reaction in the presence of Hg(0). The negative results observed from the heterogeneity experiments (hot filtration and Hg(0) poisoning) suggest that the solid catalyst could not be retrieved and no heterogeneous metal leaching occurred during the production of cyclic carbonate.

4. Conclusions

Herein, we successfully prepared $FeNi_3/DFNS/salen/Pd(II)$ MNPs. Additionally, the catalyst was characterized using various techniques, including XPS, XRD, SEM, TGA, TEM, EDX, VSM, ICP, and BET analyses. The as-synthesized $FeNi_3/DFNS/salen/Pd(II)$ MNPs are a novel stable, low-cost and non-toxic catalytic system for the synthesis of cyclic carbonate. The nanocomposite, due to its superparamagnetic nature, particularly, could be easily separated from the reaction mixture. Therefore, this catalyst did not change its reaction states, and its catalytic activity and selectivity were maintained for 10 consecutive runs without the need for reactivation, which can alleviate environmental and economic issues. Besides, the hot filtration experiments and mercury poisoning confirmed the heterogeneous nature of the catalyst and its negligible metal leaching.

Conflicts of interest

There are no conflicts to declare.

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