

FULL PAPER

Copper supported on N-heterocyclic carbene-functionalized porous organic polymer for efficient oxidative carbonylation of methanol

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A new heterogeneous catalyst for the oxidative carbonylation of methanol to dimethyl carbonate based on copper coordinated in N-heterocyclic carbene-functionalized porous organic polymer (Cu@PQP-NHC) was presented. The solid catalyst that featured relatively large surface area, hierarchical pore structure, and excellent swelling property, was prepared via a facile copolymerization reaction of tetra-vinylphosphonium salt and bis-vinylimidazolium salt, followed by successful immobilization of CuCl. Accordingly, the resulting Cu@PQP-NHC showed excellent catalytic performance for the oxidative carbonylation of methanol. A 10 mmol/l of Cu usage was sufficient for 9.3% conversion of methanol with a high TOF number of 57 h⁻¹. Importantly, the catalyst was easily recovered by simple centrifugation, and could be reused up to 10 consecutive recycles without obvious loss of its initial activity. Also, the solid catalyst showed negligible Cu leaching during the recycling, and 99% Cu species was still retained after reusing 10 times. The results in this study highlights the advantages of porous organic polymer supported NHC-Cu catalyst as a highly active and stable heterogeneous catalyst, providing a promising route for the synthesis of dimethyl carbonate.

KEYWORDS

copper, dimethyl carbonate, N-heterocyclic carbene, oxidative carbonylation, porous organic polymers

1 | INTRODUCTION

With the growing concerns about sustainable environment, green and eco-friendly synthesis of organic chemicals that minimizes the use of toxic substances, has attracted continuous and increasing attention.^[1,2] Dimethyl carbonate (DMC) is an important green

chemical that has been utilized widely as carbonylation and methylation agent, as well as green solvent in the synthetic chemistry.^[2,3] Actually, DMC can also be used as fuel additive and important building block for the synthesis of polycarbonate and polyurethane.^[4,5] In virtue of the wide industrial applications, a number of synthetic routes of DMC, including phosgenation of methanol,^[6]

oxidative carbonylation of methanol with CO and O₂,^[7] carboxylation from CO₂ and methanol,^[8] urea methanolysis^[9] and transesterification,^[10] have been developed. Among these methods, oxidative carbonylation of methanol is an attractive route because of the low prices and high activity of CO and O₂, the good atom economy (87%), and the green byproduct (water).

CuCl was used as an active and industrial catalyst for the oxidative carbonylation of methanol.^[11] However, the homogeneous CuCl system suffered from some drawbacks, such as the problems of catalyst recovery and reuse, equipment corrosion, and catalyst deactivation.^[12,13] To a certain extent, these drawbacks hamper the large-scale production of DMC via the oxidative carbonylation route. To address these issues, a number of immobilized copper complexes^[13–15] and Cu nanoparticles^[16–18] have been developed in the past two decades. Due to these efforts, the problems of catalyst recovery and deactivation as well as equipment corrosion have been alleviated to some extent. However, the efficiency and reusability of the currently available heterogeneous catalysts are still unsatisfactory. Therefore, it is still a challenge to develop the highly active and stable heterogeneous catalysts for the oxidative carbonylation of methanol.

Porous organic polymers (POPs), featuring designable chemical structure and large surface areas, have recently aroused great interest as attractive materials for developing heterogeneous catalysts.^[19,20] Nowadays, a number of synthetic methods, such as free radical polymerization, Friedel-Crafts reactions and Sonogashira coupling, have been developed for the preparation of POPs.^[21] Previous results suggested that POPs prepared by the solvothermal and free radical polymerization method have hierarchical pore structures, flexible frameworks, and excellent swelling properties.^[22–25] Consequently, these properties endow the porous catalysts with some characters of quasi-homogeneous catalysis, and thus, some of these catalysts showed comparable, or even higher catalytic activities than their homogeneous analogues.^[24,25] With this background in mind, we recently developed a phenanthroline-functionalized porous organic polymer supported copper catalyst (Cu@PCP-Phen) via a solvothermal and free radical polymerization method.^[26] The resulting Cu@PCP-Phen catalyst displayed high catalytic performance for the oxidative carbonylation of methanol, with which 6.2% conversion of methanol and a high TOF of 38.1 h⁻¹ was obtained at 120 °C for 2 hr.

As a valuable kind of organic ligands, N-heterocyclic carbene-metal (NHC-M) complexes have been extensively utilized as stable and active catalysts for a great

variety of organic reactions.^[27–29] To facilitate the product separation and catalyst recovery, a large number of supported NHC-M,^[30] such as organic polymer immobilized NHC-M,^[31,32] inorganic silica immobilized NHC-M,^[33] and POPs immobilized NHC-M,^[34–37] have also been successfully developed. Among these immobilized catalysts, POPs supported NHC-M catalysts are particularly appropriate for catalyzing liquid organic reactions because of their high surface areas and easy accessibility towards organic substrates.^[37] Recently, a number of POPs supported NHC-M catalysts have been developed via Friedel-Crafts reactions.^[34–37] However, up to date, POPs supported NHC-M catalysts that prepared by solvothermal and free radical polymerization method have been seldomly explored. On the other hand, NHC-M complexes have displayed high activities in various carbonylation reactions,^[38] nevertheless, their applications in the oxidative carbonylation of methanol to DMC have been rarely reported.

In continuation of our research interest in oxidative carbonylation reactions,^[13,26,39] herein, we designed a new porous organic polymer supported Cu catalyst (Cu@PQP-NHC) for the oxidative carbonylation of methanol. The Cu@PQP-NHC catalyst was prepared by a facile solvothermal and free radical copolymerization of tetra-vinylphosphonium salt and bis-vinylimidazolium salt, followed by complexation with CuCl. Characterization results suggested that the prepared catalyst featured relatively large surface areas, hierarchical pore structure, and excellent swelling property. These properties enabled the Cu@PQP-NHC catalyst behave as a highly active and recyclable solid catalyst for the oxidative carbonylation of methanol to DMC.

2 | EXPERIMENTAL

2.1 | Materials

1-Vinylimidazole, 4-bromostyrene, dibromomethane, phosphorus trichloride, 4-vinylbenzyl chloride (90%), tetrahydrofuran, and 2,2'-azobis(2-methylpropionitrile) (AIBN) were purchased from Energy Chemical (Shanghai) Co. Ltd. Methanol, tetrahydrofuran and 1-vinylimidazole were analytical reagents. CO and O₂ were supplied by a local company. The tetra-vinylphosphonium salt, 4-vinylbenzyl-tris(4-vinylphenyl)-phosphonium chloride (QP), was synthesized via the reaction between 4-vinylbenzyl chloride and tris(4-vinylphenyl)-phosphine.^[40] Bis-vinylimidazolium salts ([C₁DVIM]Br) was prepared via the reaction of 1-vinylimidazole and dibromomethane.^[41]

2.2 | Synthesis of PQP-NHC support

NHC functionalized porous organic polymer precursor (PQP-NHC) was prepared via a solvothermal and free radical copolymerization of $[C_1DVIM]Br$ and QP in a 100 ml Teflon autoclave. Generally, the autoclave containing $[C_1DVIM]Br$ (0.85 g, 2.3 mmol), QP (1.15 g, 2.3 mmol), AIBN (50 mg) and methanol (20 ml) was stirred at room temperature for 30 min. Then, the autoclave was heated in an oven at 100 °C for 24 hr. After the polymerization reaction, a solid monolith (Figure S1) was obtained. The resultant solid was washed with ethanol for three times, dried under vacuum to obtain a pale-yellow solid. The obtained solid was denoted as PQP-NHC (2.04 g). Elemental composition of PQP-NHC: C, 62.63%; N, 6.46, H, 4.86%.

2.3 | Preparation of Cu@PQP-NHC

In a typical procedure, NaO^tBu (192 mg, 2 mmol) was added to a suspension mixture of PQP-NHC (1.0 g) in DMF (40 ml). After stirring at room temperature for 1 hr and addition of CuCl (50 mg), the mixture was magnetically stirred in a pre-heated oil bath at 80 °C for 6 hr. Then, the resulting yellow precipitate, denoted as Cu@PQP-NHC, was isolated by filtration, washed with ethanol, and then dried under vacuum.

2.4 | Catalytic measurements

Oxidative carbonylation of methanol was performed in a high-pressure stainless-steel autoclave. General, Cu@PQP-NHC (205 mg) and methanol (10 ml) was added into the autoclave. After pressurizing with CO and O_2 to 30 bar ($P_{CO}:P_{O_2} = 2:1$), the autoclave was heated to the setting reaction temperature for 2 hr. During the reaction, a total pressure of 30 bar was maintained by supplementing CO and O_2 . The resulting reaction mixture was separated by centrifugation, the recycling solid was washed with chloroform. For recycling experiments of the catalyst, the reaction was scaled-up. Typically, Cu@PQP-NHC (615 mg) and methanol (30 ml) was added into the stainless-steel autoclave. After the catalytic reaction, the solid catalyst was separated by centrifugation, washed with chloroform for three times, dried at 60 °C in vacuum, and then engaged in a new catalytic run.

Synthesis and catalytic performance of CuCl/NHC were carried out as follow. Generally, bis-vinylimidazolium salt ($[C_1DVIM]Br$, 36.2 mg, 0.1 mmol), CuCl (9.9 mg, 0.1 mmol), NaO^tBu (19.2 mg, 0.2 mmol),

and methanol (10 ml) were added into the autoclave. Then, the reaction mixture was stirred at 80 °C for 6 hr to generate CuCl/NHC in-situ. After cooling to room temperature, the autoclave was pressurized with CO and O_2 to 30 bar ($P_{CO}:P_{O_2} = 2:1$). Then, the autoclave was heated to 120 °C for 2 hr. During the reaction, a total pressure of 30 bar was maintained by supplementing CO and O_2 . The resulting liquid mixture was analyzed qualitatively by GC.

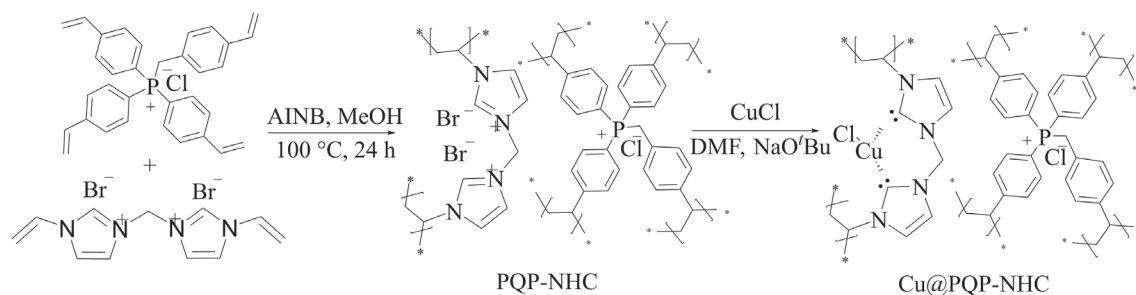
2.5 | Characterization

Inductively coupled plasma atomic emission spectroscopy (ICP, PerkinElmer Optima 8000) was used to analyze the content of copper species. Fourier Transform Infrared Spectroscopy (FT-IR) of the monomers and prepared samples were examined under ambient conditions by a Bruker Equinox 55 FT-IR spectrophotometer. Surface composition and state of Cu species were determined by X-ray photoelectron spectroscopy (XPS, VG multilab 2000 spectrometer). Elemental analysis of the samples was collected on an Elementar Vario MICRO Elemental analyzer, the sample was degassed at 90 °C before the measurements. Solid-state ^{13}C NMR spectrum was carried out on a Bruker AVANCE III 600 Bruker spectrometer. Specific surface areas of the samples were performed by a Micrometrics ASAP 2020 surface area analyzer system at 77 K, the sample was vacuum dried at 90 °C for 12 hr before analysis. The size and morphologies of obtained samples were observed with SEM and TEM over the Hitachi S-4800 and FEI Tecnai G2 F30 instruments, respectively. Thermogravimetric analysis (TGA) of the sample was carried out with a NETZSCH STA 449 F5 instrument. Quantitative analysis of the reaction mixture was performed on a gas chromatograph (Scientific™ TRACE™ 1310 apparatus). The chromatographic conditions have been carefully described in our previous report.^[26]

3 | RESULTS AND DISCUSSION

3.1 | Synthesis and characterization of the catalyst

Copper supported on N-heterocyclic carbene-functionalized porous organic polymer (Cu@PQP-NHC) was prepared by a solvothermal copolymerization of QP and $[C_1DVIM]Br$ monomers, followed by complexation with CuCl (Scheme 1). The *tetra*-vinylphosphonium salt monomer acted as a crosslinking agent,^[42,43] while the *bis*-vinylimidazolium salt monomer was used as the



SCHEME 1 Synthetic scheme of Cu@PQP-NHC

precursor of NHC ligand. ICP analysis is suggested that the Cu content in Cu@PQP-NHC was 3.10 wt%.

The porous properties of PQP-NHC and Cu@PQP-NHC were analyzed by nitrogen sorption analysis (Table 1). PQP-NHC had a BET surface area of $323 \text{ m}^2 \cdot \text{g}^{-1}$ and a pore volume of $0.71 \text{ cm}^3/\text{g}$. The immobilization of CuCl resulted in an obvious decrease of surface area and pore volume. Nitrogen sorption isotherms of PQP-NHC and Cu@PQP-NHC in Figure 1 suggested the samples exhibited similar sorption behavior. At low relative pressure regions ($P/P_0 < 0.01$), the steep steps of nitrogen gas uptake indicated the filling of micropore. At $P/P_0 = 0.6\text{--}1.0$ regions, the obvious hysteresis loops suggested the presence of mesopore. At high relative pressure regions ($P/P_0 = 0.9\text{--}1.0$), the sharp rise of gas uptake curves illustrated a certain amount of macropores. These findings indicated the hierarchical pore structure of the prepared samples. Moreover, these results coincided well with pore-size distribution curve of Cu@PQP-NHC (insert). For solid catalyst, the presence of hierarchical pores would be essential to ensure the favorable catalytic performance because these structures facilitate mass transport of reactants and products.^[35–37]

The morphology of PQP-NHC and Cu@PQP-NHC was characterized by SEM and TEM. SEM images in Figure 2(a) and (b) implied that PQP-NHC and Cu@PQP-NHC had similar porous morphology which was composed of small and loosely aggregated particles. TEM images of PQP-NHC and Cu@PQP-NHC in Figure 2(c) and (d) further confirmed the porous and loosely packed morphology of the samples. In addition,

TABLE 1 Textural properties of the prepared catalyst

Entry	Sample	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore volume (cm^3/g) ^a	Average pore radius (nm) ^b
1	PQP-NHC	323	0.71	6.7
2	Cu@PQP-NHC	191	0.50	4.9

^aSingle point adsorption total pore volume of pores at $P/P_0 = 0.95$.

^bAdsorption average pore diameter (4 V/A by BET).

these findings also suggested that no obvious morphology change occurred after immobilizing the copper species.

FT-IR spectra of monomers and the prepared samples were depicted in Figure 3. FT-IR spectra of PQP-NHC and Cu@PQP-NHC in Figure 3(c) and (d) showed the presence of C-H stretching vibrations (2930 and 2850 cm^{-1}) of the saturated methylene ($-\text{CH}_2-$). Compared to the monomers in Figure 3(a) and (b), the C-H ($>3000 \text{ cm}^{-1}$) vibrations of the terminal $-\text{C}=\text{CH}_2$ groups were absent in Figure 3(c) and (d). These findings suggested that the free-radical copolymerization reaction of the monomers was finished. In addition, PQP-NHC showed a characteristic peak of imidazolium salts at around 1170 cm^{-1} , and this band was obviously weakened in spectrum of Cu@PQP-NHC. This should be attributed to the formation NHC-metal complexes.

Solid-state ^{13}C NMR spectra of PQP-NHC and Cu@PQP-NHC in Figure 4 displayed a series of bands at around $120\text{--}152$ and $20\text{--}60$ ppm. The bands at around $120\text{--}152$ ppm corresponded to aromatic carbons of the solids, while the bands at around $20\text{--}60$ ppm should be assigned to the polymerized vinyl carbons.^[23–25] Compared to PQP-NHC, a small band at 188.5 ppm was

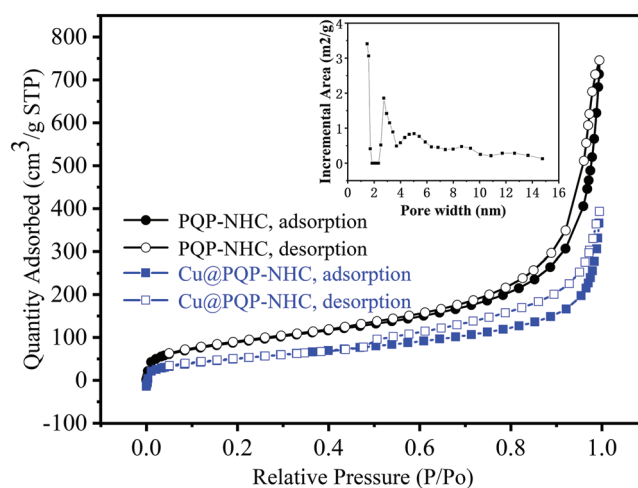


FIGURE 1 Nitrogen adsorption–desorption isotherms of PQP-NHC and Cu@PQP-NHC, and pore size distribution curve (inset) of Cu@PQP-NHC calculated by NLDFT method

FIGURE 2 SEM images of (a) PQP-NHC and (b) Cu@PQP-NHC, TEM images of (c) PQP-NHC and (d) Cu@PQP-NHC

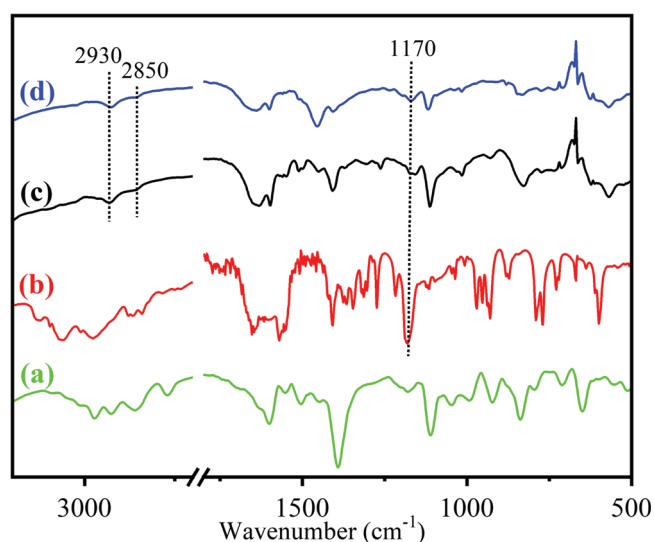
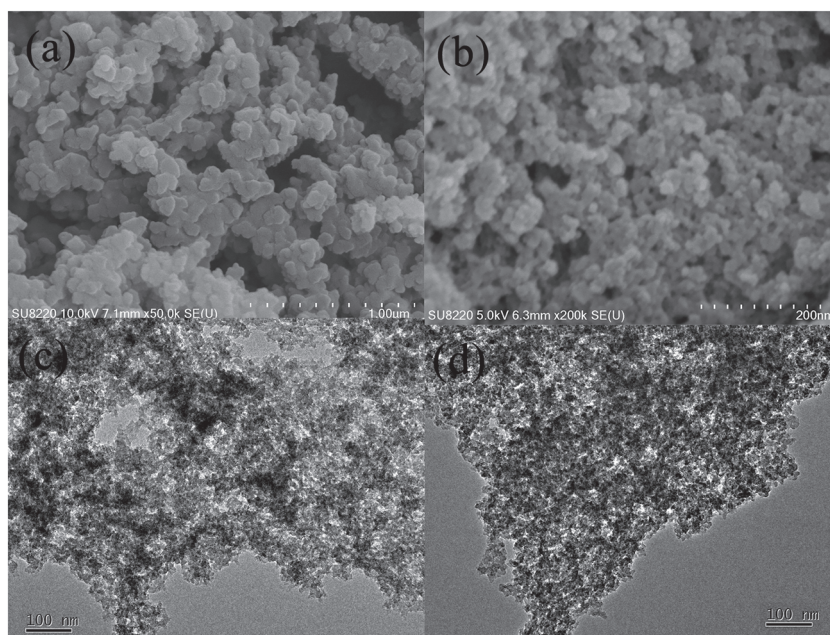


FIGURE 3 FT-IR spectra of (a) QP, (b) [ClDVM]Br, (c) PQP-NHC, and (d) Cu@PQP-NHC

present in Cu@PQP-NHC. This band might be attributed to signals of C_{NHC} .^[37]

XPS analyses of PQP-NHC and Cu@PQP-NHC were studied to gain insight into the structural information and states of Cu species. XPS full spectrum of Cu@PQP-NHC in Figure 5(a) indicated the presence of P, Cl, C, N, Br, and Cu elements. Compared to the spectrum of PQP-NHC, the presence of Cu species and significant decrease of Br element should be attributed to the formation of NHC-Cu complexes in Cu@PQP-NHC. $Cu2p_{3/2}$ spectrum of Cu@PQP-NHC in Figure 5(b) could be deconvoluted into two bands, centered at 934.3 and 932.7 eV, respectively. The small band at 934.3 eV combined with the satellite peak (938–947 eV) could be assigned to Cu^{2+} ,^[44] while

the band at 932.7 eV could be attributed to Cu^+ .^[13] As estimated by measuring the relative proportion of band areas, the molar ratio of Cu^+/Cu^{2+} in Cu@PQP-NHC was about 2.0, suggesting the partial oxidation of Cu^+ species during the immobilization process.

Thermogravimetric analysis of Cu@PQP-NHC was operated at a heating rate of $10\text{ K}\cdot\text{min}^{-1}$ and a dynamic argon atmosphere. As depicted in Figure 6, the initial weight loss that occurred at $25\text{--}150\text{ }^\circ\text{C}$ should be mainly ascribed to the removal of guest molecules. The rapid weight losses took place at above $200\text{ }^\circ\text{C}$, suggesting that Cu@PQP-NHC could be stable at least up to a temperature no less than $200\text{ }^\circ\text{C}$.

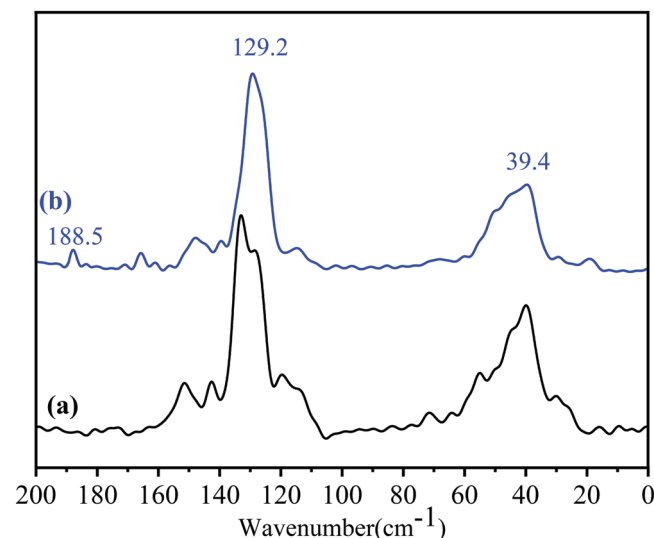


FIGURE 4 Solid-state ^{13}C NMR spectra of (a) PQP-NHC and (b) Cu@PQP-NHC

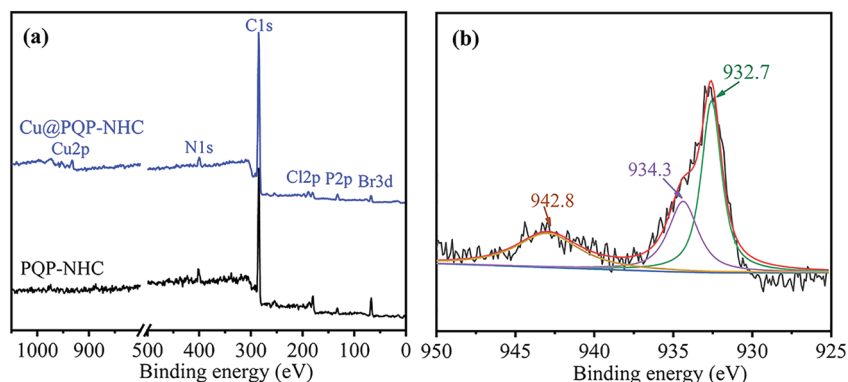


FIGURE 5 XPS spectra of the Cu@PQP-NHC sample, (a) full spectrum, (b) Cu2p spectrum

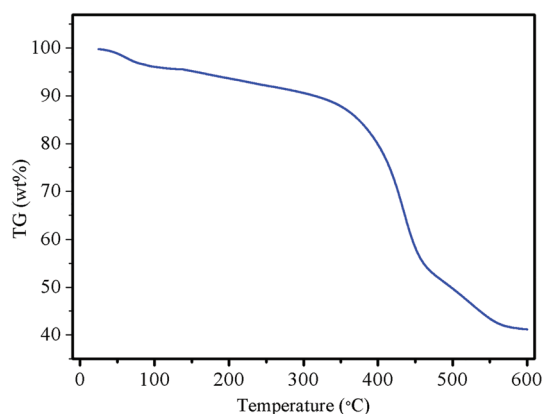


FIGURE 6 TGA curve of the Cu@PQP-NHC sample

3.2 | Catalytic performance

Catalytic performance of the obtained Cu@PQP-NHC was then studied for the oxidative carbonylation of methanol with CO and O₂. The results in Table 2 suggested that Cu@PQP-NHC was an active catalyst for the carbonylative synthesis of DMC. After reacting at 120 °C for 2 hr, a 10 mmol/l of Cu dosage was sufficient for promoting 9.3% conversion of methanol with a high TOF number of 57.0 h⁻¹ (Table 2, entry 1). The TOF number of Cu@PQP-NHC was about 2.4 times of that of commercial CuCl (Table 2, entry 2). To further investigate the promotion effect of the NHC ligand, the activity of homogeneous CuCl/NHC was tested. Obviously, the presence

of the NHC ligand led to superior catalytic activity (Table 2, entry 3). The catalytic activity of the PQP-NHC support was also tested under the reaction conditions. No catalytic activity was observed, suggesting that the Cu species were the active components of Cu@PQP-NHC catalyst (Table 2, entry 4).

Next, the effect of reaction temperature on the catalytic activity of the Cu@PQP-NHC catalyst was investigated over the range of 100–140 °C. As shown in Figure 7, with the temperature rising from 100 to 120 °C, the conversions of methanol and TOF numbers gradually increased. Meanwhile, about 99.3% selectivity of DMC

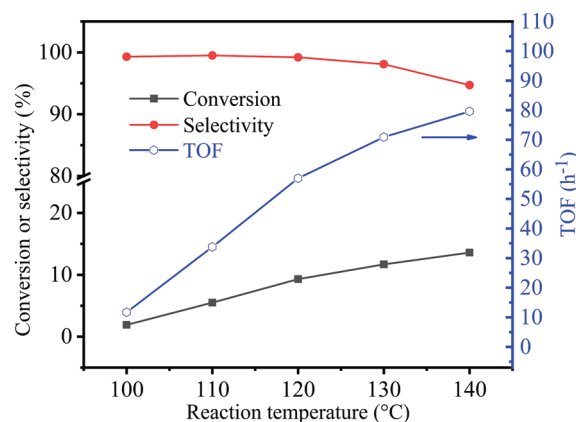


FIGURE 7 Effect of the reaction temperature. Reaction conditions: Cu@PQP-NHC (205 mg), methanol (10 ml), CO (20 bar), O₂ (10 bar), 2 hr, stirring speed (800 rpm)

TABLE 2 Catalytic results for oxidative carbonylation of methanol^[a]

Entry	Catalyst	[Cu] (mmol/l)	Conversion (%)	Selectivity (%)	TOF (h ⁻¹)
1	Cu@PQP-NHC	10	9.3	99.2	57.0
2	CuCl	10	4.2	91.3	23.7
3	CuCl/NHC	10	10.8	98.8	65.9
4 ^b	PQP-NHC	-	-	-	-

^aReaction conditions: catalyst, methanol (10 ml), CO (20 bar), O₂ (10 bar), 120 °C, 2 hr, stirring speed (800 rpm).

^bPQP-NHC (205 mg).

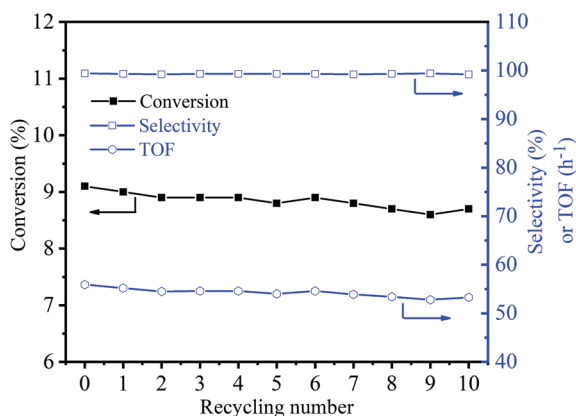


FIGURE 8 Recycling of the Cu@PQP-NHC catalyst for the oxidative carbonylation of methanol. Reaction conditions: Cu@PQP-NHC (615 mg), methanol (30 ml), CO (20 bar), O₂ (10 bar), 120 °C, 2 hr, stirring speed (800 rpm)

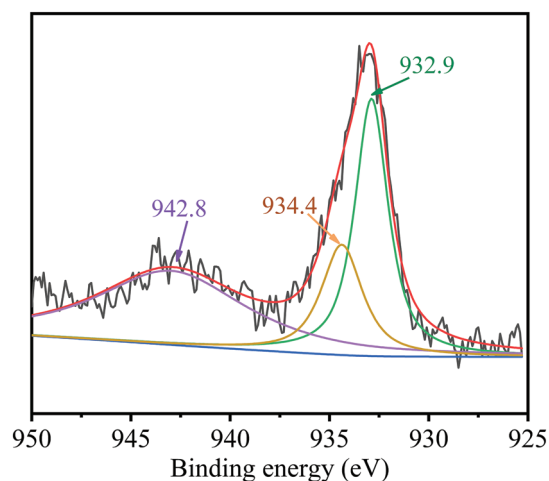


FIGURE 9 Cu_{2p_{3/2}} XPS spectrum of the recycling Cu@PQP-NHC after reusing 10 times

was maintained. Further increasing the reaction temperature to above 120 °C, a slight decrease in the selectivity of DMC was observed with methyl formate produced as a main byproduct, although a higher conversion of methanol was observed.

Then, the stability and recyclability of the Cu@PQP-NHC catalyst was evaluated. To facilitate the recycling of the solid catalyst, the catalytic reaction was conducted in scaled-up quantities. As shown in Figure 8, with three times of methanol amount, a 9.0% conversion of methanol with 99.4% selectivity of DMC was obtained in the first catalytic run. After the reaction, the solid catalyst was separated by centrifugation, washed with chloroform, dried under vacuum, and then engaged in a next catalytic run. The results suggested that Cu@PQP-NHC exhibited excellent reusability for the oxidative carbonylation of methanol. After reusing for 10 times, Cu@PQP-NHC still afforded an 8.7% conversion of methanol and a TOF of 53.3 h⁻¹. Cu leaching in the reaction mixture was also measured by ICP. Negligible Cu leaching (<0.2 ppm) was observed for each catalytic cycle. Moreover, ICP analysis revealed that about 99% Cu species was still retained in the Cu@PQP-NHC catalyst after reusing 10 times, thus further suggesting the excellent recycling ability of Cu@PQP-NHC. Additionally, XPS analysis was used to investigate the state of Cu species in the recycled Cu@PQP-NHC. The Cu_{2p_{3/2}} spectrum in Figure 9 suggested that most of the Cu species was remain in +1 state, and the molar ratio of Cu⁺/Cu²⁺ was 2.2. Previous investigations suggested that the valence of copper species has an important influence on catalytic performance, and Cu⁺ species was more active than Cu²⁺ species.^[45–47] Thus, these results demonstrated that the Cu@PQP-NHC catalyst is a highly active, stable and recyclable catalyst for the oxidative carbonylation of methanol.

We further compared the catalytic performance of Cu@PQP-NHC with some other Cu-based catalysts that

TABLE 3 Comparing the catalytic performance of different Cu-based solid catalysts for the oxidative carbonylation of methanol in liquid phase

Entry	Catalysts	Conditions	Conv. (%)	Sel. (%)	Run	TOF(h ⁻¹)	Ref.
1	Cu@PQP-NHC	120 °C, 3 MPa, 2 hr	9.3	99.2	11	57.0	This work
2	CuCl/PS-Phen	120 °C, 3 MPa, 2 hr	15.6	96.8	7	2.32	[13]
3 ^a	Bpya-CuCl ₂	140 °C, 2 hr	1.76	91.8	3	-	[14]
4	SBA-diamide-CuCl	120 °C, 3 MPa, 5 hr	22.1	99.2	4	~5.3	[15]
5	Cu/NG	120 °C, 3 MPa, 1.5 hr	3.1	97.6	5	16.9	[16]
6	Cu@HCS-5	110 °C, 3 MPa, 1.5 hr	3.7	90.4	5	23.8	[17]
7	Cu/NCNT200	110 °C, 3 MPa, 1.5 hr	2.44	97.8	4	17.6	[18]
8	Cu@PCP-Phen	120 °C, 3 MPa, 2 hr	6.2	99.5	7	38.1	[26]
9	Cu/rGO-CB	120 °C, 3 MPa, 1.5 hr	5.6	97.4	5	~27	[48]

^aCu usage (150 mmol/l).

has been reported previously. The results in Table 3 indicated that the prepared Cu@PQP-NHC exhibited much better catalytic activities and reusability than previously reported solid Cu catalysts. In term of the physicochemical properties of the Cu@PQP-NHC, its superior catalytic performance should be assigned to the relatively large surface areas, hierarchical pore structure, and excellent swelling property.

4 | CONCLUSIONS

In summary, a promising approach for the oxidative carbonylation of methanol to dimethyl carbonate was developed using copper coordinated in N-heterocyclic carbene-functionalized porous organic polymer as a robust and active catalyst. The new catalyst was synthesized through a simple copolymerization and successive immobilization method. Physicochemical characterizations suggested that the prepared catalyst featured relatively large surface areas, hierarchical pore structure, and excellent swelling property. Under optimal reaction conditions, the solid catalyst displayed high catalytic activity for the oxidative carbonylation of methanol, which outperformed commercial CuCl and previously reported solid Cu catalysts. In addition, the catalyst showed negligible Cu leaching and could be reused at least 10 times without significant loss of catalytic activity. Thus, this protocol provided not only an active, robust, and recyclable solid catalyst for the oxidative carbonylation of methanol to dimethyl carbonate, but also paved a way for developing efficient heterogeneous catalysts for other oxidative carbonylation reactions.

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