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Mesoporous Imine-Based Organic Polymer: Catalyst-Free Synthesis in Water and Application in CO_2 Conversion

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Mesoporous imine-functionalized organic polymer (Imine-POP) was prepared based on the reaction of aryl ammonium salt with aromatic aldehyde in water without any catalyst and template. Pd coordinated Imine-POP exhibited high catalytic activity for N-formylation of amines with CO_2/H_2 at 100 °C, affording a series of formamides in high yields.

As a renewable and environment-friendly C1 building block, carbon dioxide (CO_2)-involved synthesis of chemicals has attracted much attention because it can reduce the predominant dependence on petrochemical feedstocks for chemical supply chain.[1] Formamides are a class of chemicals with widespread applications in industry, which can be used as solvents (e.g. N, N-dimethylformamide (DMF)) and raw materials for organic synthesis.[2] Although preparation of DMF from CO_2, H_2 and dimethylamine has attracted long-term interest since 1970,[3] the N-formylation of other bulky amines using CO_2/H_2 has only been realized over Ru,[4] Co,[5] Cu[6] complexes and several heterogeneous catalysts in recent years. In contrast, heterogeneous catalysts are more desirable for industrial applications owing to the convenience of recovery and recycling. The reported heterogeneous catalytic systems for N-formylation of amines with CO_2/H_2 mainly include Pd/Al_2O_3[7], Au/TiO_2[8], Pd–Au/carbon nanotubes,[9] Pd/C[10] and Ru/POP,[11] which generally made the formylation of amines proceed at temperatures >100 °C. Hence, development of heterogeneous materials for efficient N-formylation of amines with CO_2/H_2 under mild conditions are of importance for their practical applications.

In recent years, porous organic polymers (POPs) have emerged as promising materials because they can be designed with specific functionalities, and thus have wide applications in many areas due to their advantages such as permanent porosity, high surface area, good stability, good ability to complex with metal species, and so on. In particular, POPs with CO_2-philic functionalities (e.g. fluoro,[12] nitrogen-containing groups[13]) have been prepared via different strategies, which show good performances in CO_2 adsorption and conversion.[14] As heterogeneous catalysts, mesoporous structures in POPs are highly desirable because they are favourable to mass transfer.[15] To date, different approaches have been developed for the synthesis of mesoporous POPs, and in most cases metal catalysts, templates and organic solvents are required.[14b-14d, 16] For example, Dai's group prepared mesoporous phenolic polymers and ionic organic networks using F127 as a soft template[17] and SiO_2 as a hard template.[18] Xiao et al. reported a solvent-mediated approach for the synthesis of mesoporous phosphine-functionalized POPs based on divinylbenzene polymerization.[19] Our group presented preparation of mesoporous Tröger's base-functionalized polymers using an ionic liquid/H_2O system.[20] The synthesis of POPs in water is seldom reported due to the limited solubility of monomers in water.[21] In contrast, preparation of mesoporous POPs without template in aqueous media can avoid utilization of toxic organic solvents, removal of template, as well as tedious operation and posttreatment, which may provide green route for the preparation of POPs.

Herein, we present a novel approach to prepare imine-based POP (**Imine-POP**) with mesoporous structure based on the reaction of aryl ammonium salt with aromatic aldehyde in water without any catalyst or template. The resulting polymer had surface area of 194 $m^2\ g^{-1}$ dominated from the mesopores (2-30 nm). The presence of imine groups made the polymer be able to chelate with Pd species, and the resultant Pd-immobilized **Imine-POP** (**Imine-POP@Pd**) showed good catalytic activity together with high stability and easy recyclability for the N-formylation of amines with CO_2/H_2 at 100°C.

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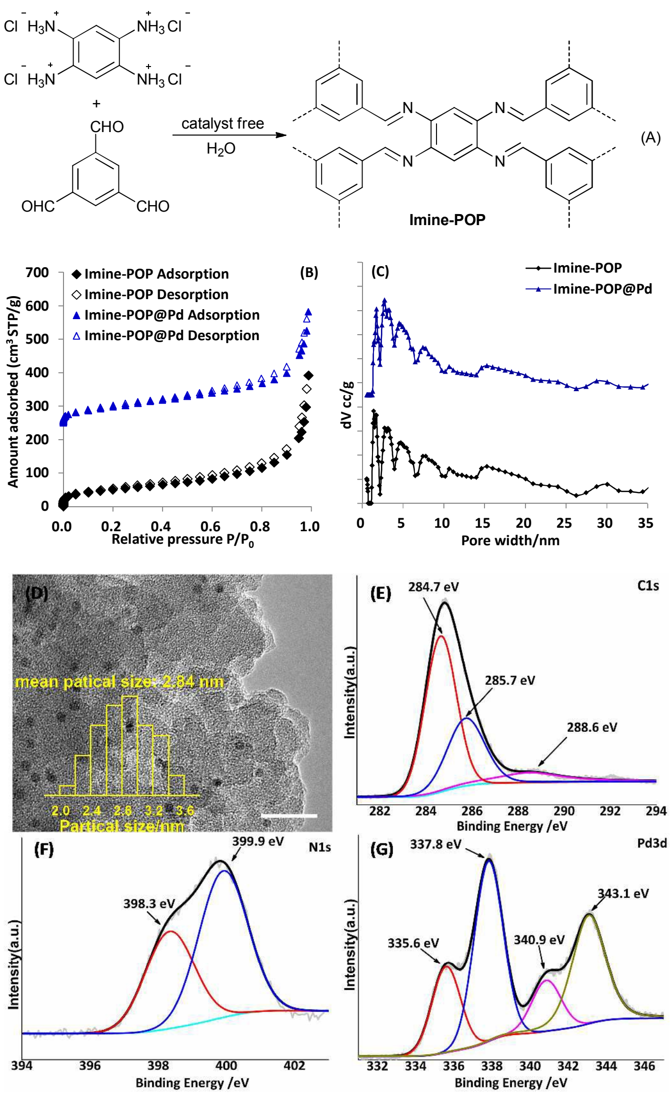

Figure 1 (A) Synthetic route for **Imine-POP**. (B) Adsorption and desorption isotherms of N_2 at 77 K. (C) pore size distributions based on the calculation results of the NLDFT method for **Imine-POP** and **Imine-POP@Pd**. (D) (HR)TEM image of **Imine-POP@Pd**. Map of Pd particle size distribution was obtained by counting 100 particles. Scale bar 25 nm (E) XPS spectra of C1s, (F) N1s and (G) Pd3d for **Imine-POP@Pd**.

As illustrated in Figure 1A, **Imine-POP** was synthesized via the reaction of 1,2,4,5-benzenetetramine tetrahydrochloride and benzene-1,3,5-tricarbaldehyde under hydrothermal condition without any catalyst or additive (For detailed synthetic procedure, see ESI). The resultant sample was in the form of loose brown powder, and did not dissolve in common solvents, such as H_2O, ethanol, DMF, tetrahydrofurane (THF) and so on. To verify the chemical structure of **Imine-POP**, a model reaction was firstly conducted using 1,2-benzenediamine dihydrochloride and benzaldehyde as substrates under hydrothermal condition, and N,N-dibenzylidenebenzene-1,2-diamine was obtained (for details, see ESI), indicating the formation of imine bond. The successful formation of the imine frameworks in **Imine-POP** was further confirmed by Fourier-transformed infrared (FT-IR) analysis and cross-polarization magic-angle spinning (CP/MAS) ^{13}C NMR analyses. In the FT-IR spectrum (Figure S1, ESI), the absorption bands of the aromatic ring were located in the range of 1450-1600 cm^{-1}, and the characteristic band at 1697 cm^{-1} belonged to the imine group within the backbone. The two bands at 3159 and 3346 cm^{-1} were probably ascribed to the unreacted amino/ammonium groups and the formed hydroxyl groups during the hydrothermal procedure, respectively. In the CP/MAS ^{13}C NMR spectrum (Figure S2, ESI), the chemical shifts in the range of 133.2~141.3 ppm were attributed to the aromatic carbons in the backbone. The signal at 151.9 ppm belonged to the carbon of imine bond. The powder X-ray diffraction (PXRD) pattern exhibited amorphous nature of the polymer (Figure S3, ESI). The morphology of the material was observed by field-emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Figure S4, ESI), which showed that the sample was composed of tiny particles with irregular shapes and sizes. The thermogravimetric analysis (TGA) results indicated that the material was stable in air up to 350 °C, which meets the demand for potential applications in catalytic CO_2 conversion (Figure S5, ESI).

Textural information on **Imine-POP** was obtained by N_2 sorption analysis. The N_2 sorption isotherms of the polymer exhibited combined features of type I and type IV with two evident steep steps in the regions of P/P_0=0~0.01 and 0.80~0.98, suggesting the coexistence of micro- and mesopores (Figure 1B). Based on the calculated result of the non-local density functional theory method (NLDFT), it is clear that micropores with size around 1.4 nm and mesopores with pore diameters in the range of 2–30 nm were existent in **Imine-POP** (Figure 1C). The BET surface area of **Imine-POP** was estimated to be 194 m^2g^{-1} with pore volume of 0.608 cm^3 g^{-1} (For BET plot, see Figure S6, ESI). Notably, mesopore played the dominant role in the pore structure of **Imine-POP**, contributing ~99% of the total pore volume (V_{micro} = 0.0028 cm^3 g^{-1}, calculated by t-plot method).

Since imine bond can chelate with metal ions,[22] **Imine-POP** was taken as the support for further metal immobilization. **Imine-POP@Pd** was prepared by treating the polymer with $Pd(OAc)_2$ in CH_2Cl_2 (for experimental details, see ESI). The content of Pd species decorated onto **Imine-POP** was 8.30 wt%, as determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis. (HR)TEM examination indicated that the Pd species were present in the form of particles with size around 2.84 nm, which were uniformly distributed on the polymer support (Figure 1C and Figure S7 in ESI). The energy dispersive spectroscopy (EDS) profile obtained during TEM observation indicated the coexistence of Pd, C, and N in the material (trace amounts of O, Cu were induced by lacey support films) (Figure S8, ESI), and compositional EDS mapping of **Imine-POP@Pd** exhibited homogeneous distribution of C, N, and Pd elements (Figure S9, ESI).

To explore the oxidation stated of Pd species, X-ray photoelectron spectroscopy (XPS) analysis was performed on **Imine-POP@Pd.** In the C1s XPS spectrum (Figure 1E), three peaks with the bonding energies (BEs) at 284.7, 286.5 and 289 eV can be deconvoluted, which can be ascribed to carbons of aromatic C, C=N bond and a small quantity of C=O bond. N1s spectrum (Figure 1F) mainly showed the presence of C=N bond with BE=398.3 eV in the backbone, and the residual –NH_3Cl group with C-N BE=399.9 eV. Correspondingly, Pd3d spectrum (Figure 1G) indicated the presence of Pd^{2+} with BEs at 337.8 and 343.1 eV together with metallic Pd° particles with BEs at 335.6

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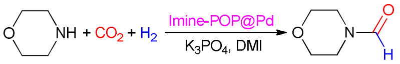
and 340.9 eV. The presence of Pd^o particles suggest that **Imine-POP** can reduce Pd^{2+} species.

The immobilization of Pd did not impact the thermal stability of **Imine-POP**, which was still stable in air up to 350 °C, confirmed by TGA analysis (Figure S5, ESI). The BET surface area of **Imine-POP@Pd** decreased to 180 m^2 g^{-1} (Figure S6, ESI) with pore volume of 0.514 cm^3 g^{-1}, slightly lower than that of **Imine-POP**. The pore size distribution curve obtained from the calculation results of NLDFT still showed the dominant existence of mesopores (Figure 1C).

Table 1 Formylation of morpholine (**1a**) with CO_2/H_2 over **Imine-POP@Pd**^{a}



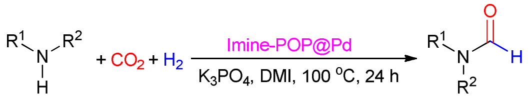
1a 2a

Entry	Change from the standard conditions	Yield/%^{b}
1	None	97
2	$Pd(OAc)_2$ 2.3 mol% instead of **Imine-POP@Pd**	93
3	**Imine-POP** instead of **Imine-POP@Pd**	0
4	K_3PO_4 0.2 mmol	88
5	No base	47
6	80 °C	85
7	60 °C	60
8	reaction time 12 h	81
9	CO_2 2 MPa + H_2 2 MPa	58
10^c	None	95

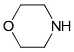
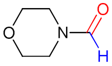
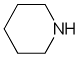
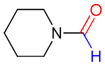
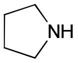
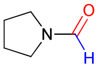
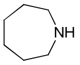
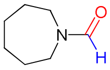
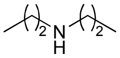
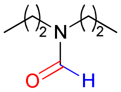
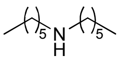
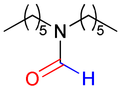
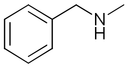
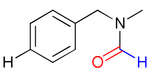
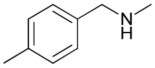
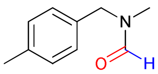
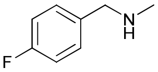
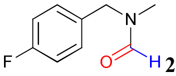
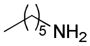
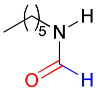
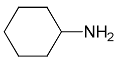
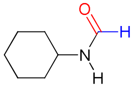
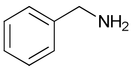
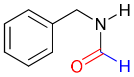
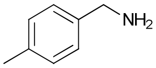
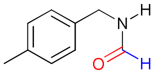
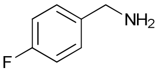
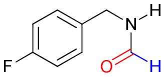
^{a} Reaction condition: **1a**, 1 mmol; **Imine-POP-Pd**, 30 mg (Pd was 2.3 mol% based on **1a**); K_3PO_4, 0.3 mmol; CO_2 3 MPa, H_2 3 MPa; DMI, 4 mL; 100 °C, 24 h. ^{b} Determined by GC using dodecane as the internal standard. ^{c}**Imine-POP-Pd** was reused for five times.

The catalytic activity of **Imine-POP@Pd** was examined by catalysing formylation of amines with CO_2/H_2. The formylation of morpholine (**1a**) was taken as a model reaction to optimize the reaction conditions (Table 1 and Table S1 in ESI). After a careful survey of the reaction parameters, N-formylmorpholine (**2a**) was obtained in a yield of 97% using 1,3-dimethyl-2-imidazolidinone (DMI) as the solvent in the presence of K_3PO_4 at 100 °C (Table 1, entry 1). Notably, this result was even higher than that obtained over $Pd(OAc)_2$ as the catalyst (**2a** yield: 93%) (entry 1 vs 2) , and much higher than that obtained over the Pd heterogeneous catalysts decorated on other supports including Al_2O_3, TiO_2, activated carbon under otherwise identical reaction conditions (Table S1, ESI). These results indicate that the **Imine-POP** support enhanced the activity of the Pd catalyst, probably due to its mesoporous structure and the CO_2-philic nature,[24] though it showed no catalytic activity (entry 3). In addition, both the solvent and base also impacted the reaction activity. DMI was used as the reaction medium owing to its Lewis basic property and CO_2-philic nature.[23] Among the tested bases including K_3PO_4, *t*-BuOK, KOH, Cs_2CO_3, DBU, K_3PO_4 showed the best performance, and its amounts influenced the product yields(Table S1, ESI). For example, the yield of **2a** decreased to 88% as the amount of K_3PO_4 decreased to 0.2 mmol (Table 1, entry 4), while it further decreased to 47% in the absence of K_3PO_4 (entry 5). The reaction could also proceed at lower reaction temperatures (e.g., 80 and 60 °C), affording moderate yields of **2a** (85% and 60%, respectively) (entries 6 and 7). In addition, shorter reaction time (e.g., 12 h) or lower CO_2/H_2 pressures led to declined **2a** yields (entries 8 and 9). Importantly, **Imine-POP@Pd** showed good reusability, confirmed by the fact that a 95% yield of **2a** was still achieved after the catalyst was reused for five times (Table 1, entry 10; Figure S10, for experimental details, see ESI). Moreover, no Pd species were detected in the filtrate of the reaction mixture by ICP-OES, indicating the strong coordination ability of the polymer with Pd species and thus good stability of **Imine-POP@Pd**.

Table 2 Formylation of amines with CO_2/H_2 catalyzed by **Imine-POP@Pd**^{a}



1 2

Entry	Substrate	Product	Yield/%^{b}
1	 1a	 2a	97
2	 1b	 2b	92
3	 1c	 2c	94
4	 1d	 2d	84
5	 1e	 2e	70
6	 1f	 2f	84 (69 ^{c})
7	 1g	 2g	99 (79 ^{c})
8	 1h	 2h	71
9	 1i	 2i	77
10	 1j	 2j	64
11	 1k	 2k	78 (62 ^{c})
12	 1l	 2l	92 (74 ^{c})
13	 1m	 2m	69
14	 1n	 2n	48

^{a} Reaction condition: **1,** 1 mmol; **Imine-POP-Pd,** 30 mg (Pd was 2.3 mol% based on **1a**); K_3PO_4, 0.3 mmol; CO_2 3 MPa, H_2 3 MPa; DMI, 4 mL; 100 °C, 24 h. ^{b} Yields were determined by NMR using CH_3NO_2 as an internal standard. ^{c} Isolated yield. For details, see ESI.

Under the optimal reaction conditions, N-formylation of other amines was investigated, and the results are shown in Table 2. The N-

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formylation reactions proceeded smoothly for primary and secondary aliphatic amines, selectively affording the corresponding formamides **2a**~**2n** in moderate to excellent yields (48%~97%). Besides **1a**, other cyclic aliphatic amines also performed well, producing the corresponding formamides **2b**~**2d** in yields higher than 84%. Linearly aliphatic amines, di-n-propylamine **1e** and di-n- hexylamine **1f**, showed good reactivity, affording 70% and 84% yields of **2e** and **2f**, respectively. The reactivity of N-methylbenzylamine was also good, with 99% yield of **2g**. However, its derivatives with electro-donating or electro-withdrawing groups (e.g. –Me or -F) showed inferior reactivities, leading to 71% yield of **2h** and 77% yield of **2i**. Formylation of primary amines with linear chains gave **2j** in 64% yield. Cyclohexylamine also showed good reactivity, affording **2k** in 78% yield. Formylation of benzylamine performed well, producing **2l** in 92% yield, while the reactivities of its derivatives with electro-donating or electro-withdrawing groups (e.g. –Me or -F) decreased, affording moderate yields of **2m** (69%) and **2n** (48%).

The formylation mechanism of amines with CO_2/H_2 was explored. Control experiments showed that HCOOH was formed via the CO_2 hydrogenation over **Imine-POP@Pd** in the absence of amine (Figure S11, ESI), which could further react with amine to form **2a** in a yield of 93% (Scheme S1, ESI). Based on previous reports[5] and results obtained in this work, it was deduced that the N-formylation product was obtained via the **Imine-POP@Pd**-catalyzed CO_2 hydrogenation to HCOOH and the subsequent reaction of HCOOH with amine (Scheme S2, ESI).

In summary, mesoporous imine-functionalized POP was synthesized in water without any catalyst or template. The integration of imine group gave the polymer strong coordination ability with the Pd species, and the resultant Pd metalated material exhibited good catalytic performance for the N-formylation of amines with CO_2/H_2 at relatively low temperature, together with high stability and easy recyclability.

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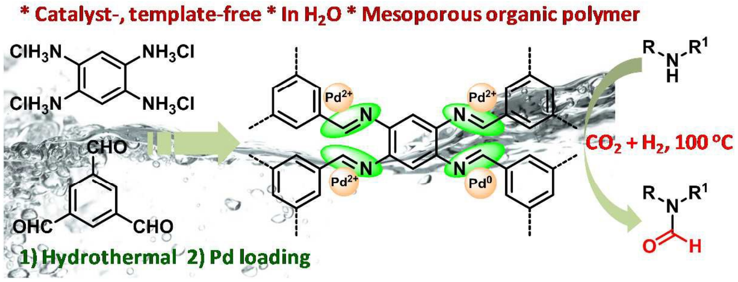

Mesoporous imine-functionalized organic polymer was prepared in water under catalyst- and template-free condition. After Pd species coordination, the resultant material exhibited high catalytic efficiency in the N-formylation of amines with CO_2/H_2.