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Microporous Polyisocyanurate and Its Application in Heterogeneous Catalysis

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Microporous and mesoporous materials, such as zeolites, activated carbon, silica and metal organic frameworks (MOFs) are widely used in catalysis, gas adsorption, storage and separations.[1] The recent development of polymer-based microporous materials may provide new opportunities in hydrogen storage and heterogeneous catalysis, as organic materials have certain advantages over other materials.[2] Microporous polymeric materials possess unique surface properties that can be tailored to facilitate chemoselective adsorption, separation and catalysis.[2,3] Although hard and soft templates have been widely used in the synthesis of porous materials,[4] a bottom-up approach facilitates the tailoring of porous materials with tailored porous structure and surface chemistry.[2,3,5] Cooper and co-workers recently reported the synthesis of conjugated microporous poly(arylene ethynylene) (PAE) by using palladium-catalyzed Sonogashira–Hagihara crossing-coupling reaction.[6] The PAE networks bridge the gap between covalent organic frameworks (COFs)[2f,g,k,l] and polymers with intrinsic microporosity (PIMs)[2a,3] or hypercrosslinked polymers (HCPs).[2c,d] Microporous polymers have also been applied in a wide range of applications, such as, gas storage and adsorption,[3a] gas separation membrane,[7] and heterogeneous catalysis.[8]

We are interested in the design and synthesis of novel covalent organic frameworks with different functional groups and controlled pore size so that the properties of porous polymers can be designed for the desired applications. Herein we report the synthesis and catalytic application of microporous polyisocyanurate (PICU) composed of rigid carbon and nitrogen networks. Although macroporous polyisocyanurates with foam-like structure have been studied,[9,10] microporous and mesoporous polyisocyanurates have not been reported. In this study, novel microporous PICUs were derived by cyclotrimerization of diisocyanate using N-heterocyclic carbene (NHC) as catalyst. The unique microporous PICU demonstrated excellent potential in reactions such as selective oxidation.

NHCs have been widely used as organocatalysts in many important transformations.[11] Recently, it was found that NHCs can efficiently catalyze cyclotrimerization of isocyanates to form a planar six-membered heterocyclic ring structure.[12] This reaction was adapted in this study to prepare porous polymer networks by replacing simple isocyanates with diisocyanates. Scheme 1 illustrates that a porous C,N organic framework could be woven by NHC organocatalysts. When rigid aryl diisocyanates were used, rigid polymer frameworks were achieved. Diisocyanate **B** was employed in this study, and various NHCs were examined in the synthesis of PICU networks. It was found that the NHCs of 1,3-bis-mesitylimidazol-2-ylidene (IMes) and 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) did not work for this synthesis. NHCs of 1,3-bis-mesityl-4,5-dihydroimidazol-2-ylidene (SIMes) and 1,3-bis-(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene (SIPr) showed low activities. In contrast, NHCs with more flexible substituents, 1,3-bis-*tert*-butyl-4,5-dihydroimidazol-2-ylidene (SI*t*Bu) displayed very high activities for this synthesis.

Typically, porous PICU was synthesized by dissolving 1 mmol of monomer in 5 mL of *N*,*N*′-dimethylformamide (DMF) in a pressure flask, and 0.02 mmol of SI*t*Bu NHC was added. The reaction flask was closed and heated to 80 °C for 24 h. The reaction can be conducted at temperatures ranging from 25 °C to 150 °C; a longer period of time would be needed for the completion of the reaction at lower temperatures. The polymer product was collected by filtration, washed, and dried in a vacuum oven. In all syntheses, quantitative yields were obtained. Owing to the low solubility of the starting materials and product, the reaction was essentially conducted under a heterogeneous condition. Unlike conventional heterogeneous catalysts, the NHC catalysts in this case might migrate onto the polymer network and initiate the next catalytic cycle. Photoacoustic Fourier

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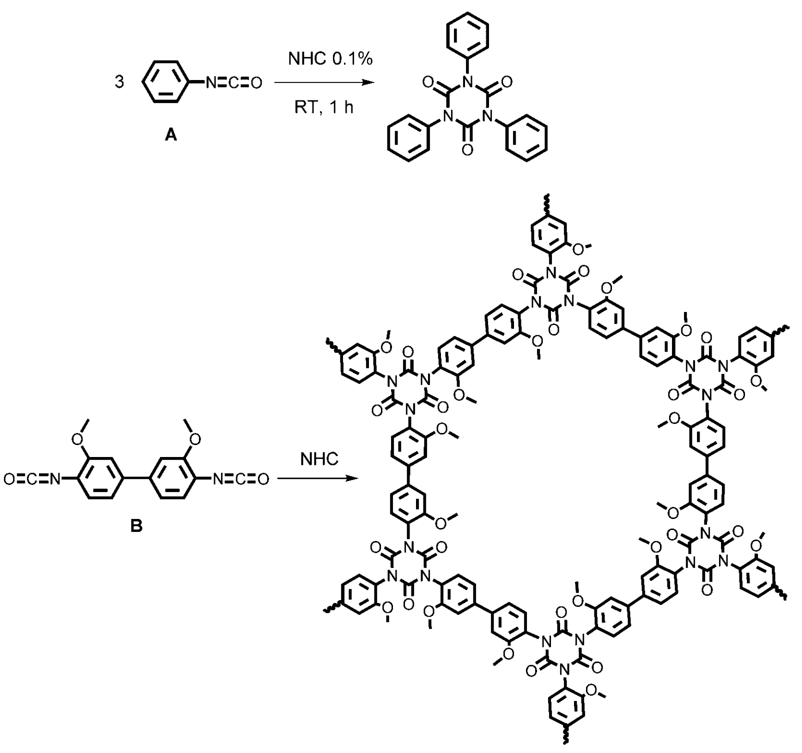


Scheme 1. Synthesis of PICU.

transform infrared (PA-FTIR) spectroscopy provided a direct method for monitoring the progress of isocyanate conversion to the polymer product. A weak peak at ~2250 cm^{-1} was observed during the synthesis, owing to the vibration of the isocyanate group (see the Supporting Information, Figure S1). This peak disappeared from the spectra of the polymer product obtained at high temperature, while a new peak emerged at 1700 cm^{-1}, owing to the presence of the -NC(O)N- group. The microstructure and morphology of polymer materials were elucidated by using scanning electron microscopy (SEM) (Figure 1). The particulate-based structure was formed at standard synthesis conditions. Thermal gravimetric analysis (TGA) indicated that the network structure of the polymers derived remained stable up to 300 °C (see the Supporting Information).

It is widely held that owing to the requirement of microscopic reversibility for crystallization, synthesis of crystalline crosslinked organic polymers would be difficult, if not impossible.[2f,6,13] We did not attain highly crystalline C,N-framework products, but generated microcrystalline polymer networks. The significantly disordered layered structure of polyisocyanurates was illustrated by transmission electron microscopy (TEM) (see the Supporting Information). The two-dimensional rigid organic sheets might only extend to limited size, and stacked in layered structures with short-range ordering. The interlayer distance was estimated by TEM to be ~3.57 Å. This value was slightly larger than graphite (3.35 Å), and Yaghi's COF-1 (3.33 Å) and COF-5 (3.46 Å); it might be the result of twisting between phenyl rings and C_3N_3 six-membered rings.[14] This new material represents a nice bridge between PIMs and COFs.

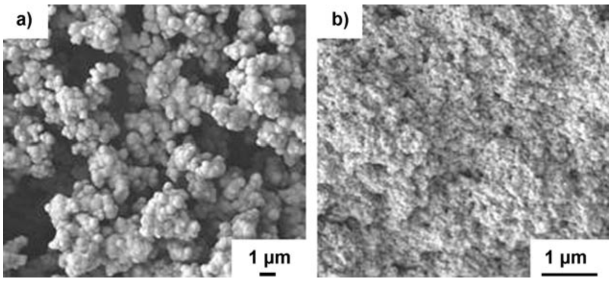


Figure 1. SEM images of PICU synthesized in DMF at a) 80 °C and b) 25 °C.

The stability and porosity of PICU were confirmed by N_2 adsorption analysis. The as-synthesized polymers were degassed at 100 °C for 16 h, and their nitrogen-adsorption isotherms were collected at 77 K. PICU showed an isotherm typical of a microporous material (Figure 2). The Brunauer–Emmett–Teller (BET) surface area of PICUs are in the range of 320 $m^2 g^{-1}$ (pore volume 0.26 $cm^3 g^{-1}$) to 569 $m^2 g^{-1}$ (pore volume 0.35 $cm^3 g^{-1}$) depending on their synthesis conditions, which were higher than many layered materials (e.g. graphite and clay), and were in the range of many zeolites, microporous carbons and other microporous polymers.[2,3,15,16] However, it was less porous as compared to Yaghi's COF-5 (1590 $m^2 g^{-1}$and 0.998 $cm^3 g^{-1}$);[2f] this could be due to its short-range order and slipped organic sheets that resulted in some inaccessible pores. The PICU was dominated by micropores of 2–20 Å (from Horvath–Kawazoe analysis), with an average pore diameter of 5 Å.

These novel materials possessed microporous network structure and isocyanurate functional units. They were expected to provide acceptor sites for both metal coordination and hydrogen-bonding interactions. PICU allowed for the phenol absorption from an aqueous solution of 2 mmol of phenol/L (see the Supporting Information). It demonstrated a superb absorption capacity of 6 mmol of phenol/g, which was higher than that of hexaazatrinaphthylene-based PIM-(Hatn) (~4.9 $mmol g^{-1}$) and carbon (0.5–4 $mmol g^{-1}$).[3a]

Given the unique properties of PICU, we have examined this new material as a catalyst support and an absorbent to concentrate reactants in aqueous solution. If successfully

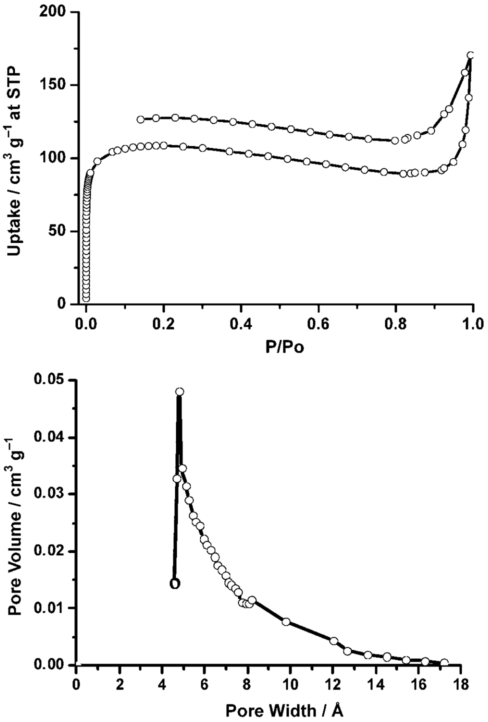


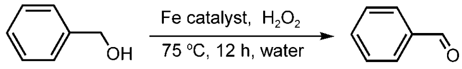
Figure 2. Nitrogen adsorption–desorption isotherm and pore size distribution of PICU.

demonstrated, such dual functionality would allow selected reactions to be run in water instead of environmentally unfriendly organic solvents. The oxidation of benzyl alcohol with H_2O_2 over iron oxide was investigated as a probe reaction.[15,16] Iron-based catalysts are inexpensive, environmentally benign, relatively non-toxic, and of interest for both bench-scale and industrial processes.[17–20] PICU supported iron catalyst (Fe/PICU) was tested in oxidation reactions in aqueous solution under mild reaction conditions.

Fe/PICU was prepared by suspending PICU in hot DMF solution of $FeCl_2$. $FeCl_2$/PICU (Fe loading = 0.25 mmol g^{-1}) was activated by H_2O_2 in hot water before it was used as oxidation catalyst. In the selective oxidation of benzyl alcohol to benzaldehyde, Fe/PICU showed excellent selectivity and activity as compared to other Fe catalysts[17] (see Table 1). Fe/PICU provided a conversion of 51 % (TON ≥ 100) with benzaldehyde selectivity of 99 % in water at a catalyst loading of 0.5 mol %. The activity and selectivity of Fe/PICU were higher than the homogeneous $FeCl_2$ catalyst (TON = 29 with 51 % selectivity) (Table 1, Entry 7), and free Fe_2O_3 nanoparticulate catalysts (3–5 nm or 50 nm) in neat benzyl alcohol system (Table 1, Entries 8–10).[17] Remarkably, Fe/PICU also displayed excellent recyclability. It could be used for at least 8 cycles without any reduction in activity and selectivity (Table 1, Entries 4–5). Control experiment with PICU (no iron salt) gave less than 5 % conversion.

Transmission electron microscopy (TEM) showed that no particles were observed in the Fe/PICU catalyst before reaction (Figure 3a and b) and after the first run (Figure 3c). Highly dispersed nanoparticles of ~1 nm were noted only after the fifth run (Figure 3d). This illustrated the ultrahigh dispersion of iron catalyst on PICU initially, and the slow aggregation to form nanoclusters only after multiple runs. It demonstrated that the microporous PICU framework with functional groups helped to stabilize iron catalyst, preventing the formation of large iron oxide particles that would result in reduced activity.

Table 1. Selective oxidation of benzyl alcohol to benzaldehyde.[a]



Entry	Catalyst	H_2O_2 [equiv]	TON[b]	Selectivity [%][c]
1	Fe/PICU	1.5	105	98
2	Fe/PICU	1.2	101	99
3	Fe/PICU	1.0	100	99
4[d]	Fe/PICU	1.2	101	99
5[e]	Fe/PICU	1.2	100	98
6[f]	Fe (2 %)/PICU	1.2	39	95
7	$FeCl_2$	1.2	29	51
8[g]	Fe_2O_3 (50 nm)	1.0	32	97[17]
9[g]	Fe_2O_3 (50 nm)	1.5	12	66[17]
10[g]	Fe_2O_3 (3-5 nm)	1.0	30	35[17]

[a] Typical reaction conditions: 20 mg of Fe/PICU (0.005 mmol of Fe), 1 mmol of benzyl alcohol, and 1–1.5 equivalents of H_2O_2 (30 wt % in water) in 1 mL of H_2O. [b] Number of moles of benzaldehyde per mole of catalyst. [c] Selectivity based on alcohol conversion, and determined by gas chromatography-mass spectrometry (GC-MS) with external standard. [d] Seventh run with recycled catalyst from Entry 2. [e] Eighth run with recycled catalyst from Entry 2. [f] 2 mol % of Fe catalyst was used. [g] Reaction conditions: 1 mol % of catalyst, neat, H_2O_2 (30 wt % in water) was added continuously over 12 h.[17]

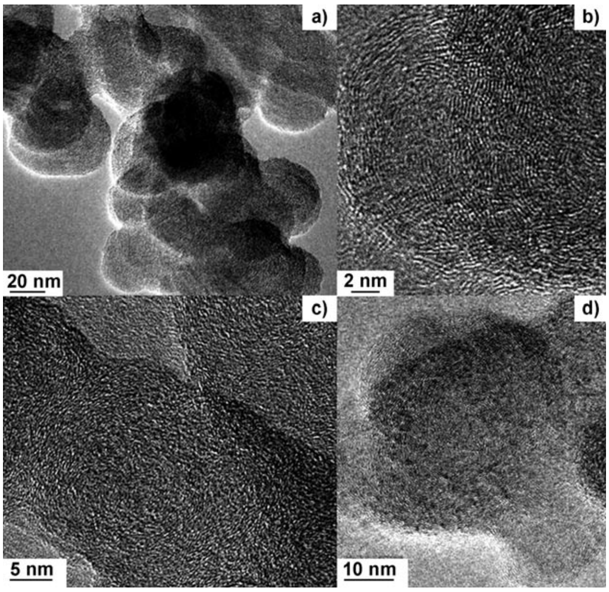


Figure 3. TEM images of Fe/PICU a,b) before reaction, c) after the first run, and d) after the fifth run.

The superior activity and selectivity of PICU could be attributed to its microporosity and excellent absorption capacity. In heterogeneous catalysis, ultrafine clusters dispersed on a suitable support would provide a higher surface area than free nanoparticles of larger sizes. In addition, the concentration of reactants was an important factor in determining the catalytic activity.[21] Benzyl alcohol could be concentrated in the micropores of PICU around the active Fe sites to further promote the catalytic conversion. High selectivity was achieved in the presence of the H_2O_2 dissolved and diluted in water. We further demonstrated that Fe/PICU offered high activity and selectivity in the oxidation of secondary benzyl alcohols to ketones and of aryl olefins to benzaldehyde (see SI for details).

In conclusion, a new method has been developed to synthesize functional microporous covalent network with NHC as the organic catalyst. The new PICU material possesses urea-type rigid functional framework, high surface area and a permanent microporous structure. It forms a layered structure with short-range order. PICU shows excellent properties in supporting metal complexes and metal particles, and has a high absorption capacity for phenol in water. Fe/PICU catalyst offers excellent activity, selectivity and recyclability in the oxidation of benzyl alcohol to benzaldehyde with H_2O_2 in water. This bifunctional system successfully concentrates the organic substrates in the PICU micropores, and stabilizes the dispersion of active iron species against aggregation. This study demonstrates the potential of a new class of microporous polymers in the catalysis of organic reactions in water.

Experimental Section

All solvents and chemicals were used as obtained from commercial suppliers, unless otherwise noted. Dry solvents and nitrogen glove box were used for the set up of reactions. PA-FTIR spectra were recorded by using a Digilab FTS 7000 FTIR spectrometer equipped with a MTEC-300 photoacoustic detector. TGA was performed by using a Perkin–Elmer Pyris-1 Thermogravimetric Analyzer. SEM images were obtained on a JEOL JSM-7400F electron microscope (10 kV). TEM experiments were conducted on a FEI Tecnai G^2 F20 electron microscope (200 kV).

Synthesis of PICU: In a glove box, **B** (980 mg, 5 mmol) was dissolved in DMF (50 mL) in a pressure flask, and SI*t*Bu (0.1 mmol, generated in situ) was added. The reaction flask was sealed, and placed in the oven at 80 °C for 3 days. PICU was collected by filtration, washed with DMF, CH_2Cl_2, and diethyl ether, and then dried in a vacuum oven. Quantitative yield of PICU was obtained.

N_2 Adsorption measurement: PICU samples were degassed at 100 °C for 16 h. N_2 adsorption isotherms were obtained at 77 K by using a Micromeritics ASAP 2020 M system.

Phenol absorption experiment: PICU (50 mg) was suspended in aqueous phenol solutions (8 mL) of various concentrations. The mixtures were stirred overnight at 25 °C. Each suspension was filtered to remove the polymer. After the necessary dilutions, the concentrations of the remaining phenol solutions were determined from their absorbance at $\lambda =$ 270 nm by UV spectrometry (see the Supporting Information, Figure S5).

Synthesis of Fe/PICU catalyst: $FeCl_2$ (63 mg, 0.5 mmol) and PICU (1 g) were mixed in DMF and stirred at 80 °C overnight. A light-yellow powder was obtained after filtration, washing and drying. The powder was suspended in water, and H_2O_2 (2 mmol, 30 wt % in water) was added. The resulting mixture was stirred at 80 °C for hours. Brownish–yellow Fe/PICU powder was obtained after filtration, washing, and drying. The TGA analysis showed a Fe loading of 0.25 mmol g^{-1}.

General procedure for oxidation reaction: Fe/PICU (20 mg, 0.005 mmol of Fe) was suspended in a reaction vial with water (1 mL). The substrate (1 mmol) and H_2O_2 (1–2 mmol, 30 wt % in water) were then added to the vial. The vial was capped and stirred at 75 °C on a hot plate for 12 h. The reaction mixture was next cooled to room temperature, and an external standard (chlorobenzene) was added. The reaction mixture was extracted by ethyl acetate, and quantitatively analyzed by GC with calibration curve.

Recycling experiment for oxidation reaction: After extraction with ethyl acetate, the reaction mixture was further washed with ether. After removing the remaining organic solvent under vacuum, the reaction mixture was used for the next run.

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