Chinese Journal of Catalysis 38 (2017) 583–588

available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Environmentally benign and economic synthesis of covalent triazine-based frameworks

Ling Zhang [a,b], Xue Liu [b], Rui-Xia Yang [b], Nian-Yu Huang [a], Wei-Qiao Deng [b,*]

[a] *Hubei Key Laboratory of Natural Products Research and Development, College of Biological and Pharmaceutical Sciences, China Three Gorges University, Yichang 443002, Hubei, China*

[b] *State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China*

ARTICLE INFO

Article history:
Received 30 November 2016
Accepted 25 December 2016
Published 5 March 2017

Keywords:
Covalent triazine-based framework
Aryl bromide
Cyanation
Potassium hexacyanoferrate(II)
Palladium acetate

ABSTRACT

Covalent triazine-based frameworks (CTFs) are important microporous materials with a wide range of applications. Here, we demonstrate an environmentally benign and economic synthetic pathway to CTFs. The monomers used for CTFs, aromatic nitriles, were obtained by cyanation using nontoxic potassium hexacyanoferrate(II) in place of commonly used toxic cyanides. Then, the CTFs were synthesized by trimerization of the corresponding cyano monomers in molten zinc chloride. A series of CTFs was synthesized, and the highest Brunauer-Emmett-Teller surface area measured in this series was 2404 m^2/g. Among the synthesized CTFs, CTF_{DCP} exhibited excellent CO_2 adsorption properties, with a CO_2 uptake of 225 mg/g at 0 °C.

1. Introduction

The field of microporous materials has recently seen remarkable development owing to the potential applications of these materials in gas storage, separation and catalysis [1–4]. Compared with traditional porous materials, organic microporous materials have the advantages of high specific surface areas, good solubility, diverse synthetic methods and wide applicability [2]. With the ever increasing sophistication of synthetic methods available for the construction of organic porous materials, porous materials with various functions can now be synthesized according to researchers' diverse needs.

Covalent organic frameworks (COFs) are a unique class of crystalline porous organic polymers with inherent porosity and periodic molecular ordering [5–7]. It is, however, difficult to construct crystalline COFs because their syntheses require reversible condensation reactions that have to be carried out under thermodynamic rather than kinetic control [8].

Covalent triazine-based frameworks (CTFs) are a special and emerging class of COFs [9] that are produced by ionothermal trimerization of aromatic polynitriles in molten $ZnCl_2$ to give triazine rings [10]. For example, the first reported CTF, CTF-1 [10], was prepared by trimerization of *p*-dicyanobenzene. CTFs are gaining an increasing amount of attention because of their excellent chemical and thermal stabilities, ultra-high Brunauer-Emmett-Teller (BET) surface areas and porosities, as well as the high amount of nitrogen functionalities in their networks. Owing to these remarkable properties, CTFs have been applied in many fields, including catalysis [11–13], gas adsorption and storage [14–16], sorbent materials [17,18], organic semiconductors [19], electrical materials [20,21] and others [22–24].

---

* Corresponding author. Tel: +86-411-84379571; Fax: +86-411-84675584; E-mail: dengwq@dicp.ac.cn

This work was supported by the National Natural Science Foundation of China (21373202, 21525315).

DOI: 10.1016/S1872-2067(17)62771-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 3, March 2017

To synthesize CTFs on a large scale for potential commercialization, an economical synthetic pathway is required. The key monomers used in CTFs are multiple cyano-substituted benzenes, but these are not available on a large scale. The traditional synthetic routes to cyano-substituted benzenes include Rosenmund von Braun reactions [25–27] from aryl halides, diazotization of anilines and the Sandmeyer reaction [28]. However, these synthetic methodologies are associated with the use of overstoichiometric amounts of toxic cyanides, such as $Zn(CN)_2$ [29], CuCN [30], KCN [31], NaCN [32] and trimethylsilyl cyanide (TMSCN) [33], as the cyanide source, which is a serious environmental concern. Recently, nontoxic potassium hexacyanoferrate(II) was introduced as a cyanation agent by Beller's group [34–36]. They demonstrated that aryl halides can react with potassium hexacyanoferrate(II) to give cyano compounds in the presence of catalytic amounts of palladium catalysts and ligands such as 1,5-bis(diphenylphosphino)pentane (dpppe), 1,1′-bis(diphenylphosphino)ferrocene (dppf), triphenylphosphine (PPh_3), tricyclohexylphosphine (PCy_3) and 2,2′-bis(diphenylphosphino)diphenyl ether (Bpephos). A drawback of this procedure is the need for expensive ligands, which not only greatly increases the cost of the experiments, but also limits the scale of the reaction. Recently, several triazine-functionalized porous polymers were synthesized using imide-functionalized 1,3,5-triazine frameworks and showed high CO_2-adsorption capacities [37,38]. Modak *et al.* [37] reported a one-pot bottom-up synthetic strategy for the triazine-functionalized porphyrin-based porous organic polymer TPOP-1, which showed a CO_2 uptake of up to 6.2 mmol/g at 3×10^5 Pa and 0 °C. Gomes *et al.* [38] reported the synthesis of the polymer TRITER-1 by condensation polymerization of 1,3,5-tris-(4-aminophenyl)triazine (TAPT) and terephthaldehyde.

In this work, we have developed a new synthetic pathway for CTFs. First, multiple cyano-substituted aromatics were synthesized using inexpensive and nontoxic $K_4[Fe(CN)_6]\cdot 3H_2O$ as the cyanide source for cyanation of aryl bromides. This reaction was catalyzed by $Pd(OAc)_2$ without addition of other ligands. Second, CTFs were synthesized by polymerization of the multiple cyano-substituted aromatics in molten $ZnCl_2$, which acts as both a catalyst and a solvent at temperatures of 400–600 °C [10]. The obtained CTFs exhibited excellent CO_2-adsorption properties.

2. Experimental

2.1. Reagents

All reagents were purchased from Alfa Aesar, J&K Scientific Ltd., Aladdin Reagent and Sigma Aldrich, and were used without further purification. 1,4-Dicyanobenzene (**1b**), 2,6-dicyanopyridine (**2b**) and 1,4-dicyanonaphthalene (**3b**) were prepared from their corresponding aryl bromides with $K_4[Fe(CN)_6]\cdot 3H_2O$ in the presence of $Pd(OAc)_2$ according to a previously reported method [34,39]. **1b**–**3b** were isolated from the reaction mixtures and characterized by ^1H NMR and ^{13}C NMR spectroscopy.

2.2. Analytical methods

GC-MS analysis was performed on a GCMS-QP2010SE spectrometer. *n*-Hexadecane was selected as the internal standard for GC-MS after optimization. The NMR spectra (^1H, 400 MHz; ^{13}C, 100 MHz) were recorded on a Bruker Mercury Plus 400-MHz spectrometer. $CDCl_3$ was used as the solvent with tetramethylsilane (TMS) as the internal standard. The synthesis of CTFs was carried out in a muffle burner (TSX1200). The specific surface area of the CTFs was measured on an adsorption instrument (Quantachrome Quadrasorb SI).

2.3. Typical procedure for palladium acetate-catalyzed cyanation of aryl bromides

Aryl bromide (6.0 mmol), $K_4[Fe(CN)_6]\cdot 3H_2O$ (2.4 mmol), Na_2CO_3 (6.0 mmol) and $Pd(OAc)_2$ catalyst (0.2 mol% relative to the aryl bromide) were mixed in NMP (12 mL) in a 25-mL flame-dried double-neck round-bottom flask and heated with stirring at 130 °C under argon. The progress of the reaction was monitored by GC-MS. At the end of the reaction, the mixture was cooled to room temperature. Samples were quenched with H_2O (or with sat. NH_4Cl when pyridines were used as substrates), and extracted with EtOAc (25 mL × 3). The organic layer was washed with water (15 mL × 3) and 5% $NH_3\cdot H_2O$ (15 mL × 2), and then dried over Na_2SO_4. Evaporation of the solvent left the crude product, which was further purified by column chromatography over silica gel (60–120 mesh) eluting with petroleum ether/ethyl acetate to afford the pure aryl nitrile.

1,4-Dicyanobenzene (**1b**, DCB). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.80$ (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 132.81, 117.00, 116.76$.

2,6-Dicyanopyridine (**2b**, DCP). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 8.15$ (dd, $J = 8.4, 7.4$ Hz, 1H), 7.99 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 139.13, 135.22, 131.29, 115.53$.

1,4-Dicyanonaphthalene (**3b**, DCN). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 8.35$ (dd, $J = 6.4, 3.2$ Hz, 2H), 7.98 (s, 2H), 7.87 (dd, $J = 6.4, 3.2$ Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 132.00, 131.09, 130.30, 126.03, 116.27, 115.20$.

2.4. Synthetic procedure for CTFs

Traditional CTF synthesis has been described elsewhere [10]. In this work, aryl nitriles (7.8 mmol) and anhydrous $ZnCl_2$ (39.0 mmol) were transferred into a quartz ampoule (15 cm^3) under an inert atmosphere. The ampoule was evacuated, sealed and heated to 400 °C for 20 h and then to 600 °C for another 20 h. The ampoule was then cooled to room temperature and opened carefully (*Caution:* the ampoule is under pressure, which is released on opening). The reaction mixture was then ground and washed thoroughly with large amounts of water to remove most of the $ZnCl_2$. It was then stirred in dilute HCl for 15 h to remove the residual salt. After this purification step, the resulting black powder was filtered, washed successively with water and THF and dried in vacuum at 120 °C. The yield of the reaction was high (> 91%) to quantitative.