

Porphyrin based porous organic polymer as bi-functional catalyst for selective oxidation and Knoevenagel condensation reactions

Arindam Modak, John Mondal, Asim Bhaumik*

Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

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ABSTRACT

Porphyrin based microporous organic polymer Fe-POP-1 has been synthesized through a facile solvothermal method involving extended aromatic substitution of pyrrole and terephthalaldehyde in the presence of Fe(III). This material has very high BET surface area and exhibits two types of catalytic sites: iron-free porphyrin moieties for base catalysis as well as Fe(III)-bound sites for selective oxidation reactions. Due to the presence of basic porphyrin macrocyclic site in Fe-POP-1, it catalyzes Knoevenagel condensation of aromatic aldehydes with malononitrile at room temperature, whereas the Fe(III)-bound site catalyzes selective oxidation of alcohols to the respective aldehyde/ketones in the presence of *tert*-butyl hydroperoxide (TBHP) as oxidant. Good reusability and excellent selectivity makes this Fe-POP-1 as a promising and efficient bi-functional heterogeneous catalyst for the production of organic fine chemicals through the environmentally benign liquid phase catalytic reactions.

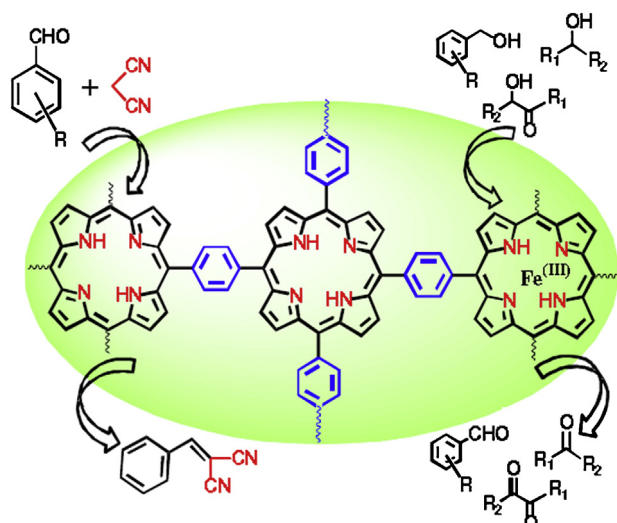
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1. Introduction

Over the past few decades porous materials have attracted widespread application in many frontline areas of science and technology, and generated immense scientific interests [1,2]. Unlike mesoporous materials with wide pore dimensions [3–6], metal organic framework (MOF) or purely organic frameworks based on micropores with restricted pore dimensions (<2 nm) have attracted much interests in the context of gas adsorption and storage [7,8]. But their potential as catalysts and catalytic supports are much less explored due to instability of their porous structure under humid atmosphere in the liquid and gas phase catalytic reaction conditions [9]. Porous organic polymers with amorphous structures are devoid of such disadvantage as they are much easier to synthesize. Thus, based on this unique structural feature several opportunity lies in microporous polymers and several reactive functional groups can be attached at the surface of this intriguing class of material. Microporous organic polymers that have attracted immense interest in recent times include conjugated microporous polymers (CMPs) [10], polymers of intrinsic microporosity (PIMs) [11], crystalline triazine-based frameworks (CTFs) [12], porous aromatic frameworks (PAFs) [13], and so on. But despite their complicated and tedious synthetic routes, and sometimes very

expensive catalysts needed for their synthesis, none of these materials have been explored in bi-functional catalytic reactions [14–17]. Selective oxidation of alcohols to carbonyl compounds is one of the most important fundamental reactions in organic chemistry, since the carbonyl group that produced is an invaluable building block for the synthesis of a variety of organic fine chemicals [18,19]. Conventional methods like Swern or Jones oxidation using stoichiometric amount of inorganic oxidizing agent (i.e., KMnO_4 , MnO_2 , CrO_3 , Br_2 , etc.) suffers from huge drawbacks like production of heavy metal wastes, eco-toxicity and poor reusability [20,21]. Heterogeneous catalyst based on Au nanoparticles [22], Pd [23], Au/Pd, Au/Pt [24], Fe [25] nanoparticles or they are dispersed over high surface area carbon or oxide supports [26], Ru and Cu [27] containing catalysts, etc. have been employed to overcome this problem. But the use of heavy toxic metals, high reaction temperatures, leaching of the metallic species from the catalyst surface to the solution, are the major drawbacks of these catalytic systems. Thus, for the development of a green and sustainable catalytic process a robust heterogeneous catalyst, which is highly reactive for the liquid phase selective oxidation reactions under mild reaction conditions in the presence of the peroxide as oxidant is very desirable [28,29]. Similarly, base catalysis is also another fascinating area of research and in this context Knoevenagel condensation has received particular attention. This reaction introduces conjugated double bonds in the aromatic compounds and solid bases like alkali or alkaline-earth-metal oxides [30] are conventionally used as catalyst for this reaction. A number of modifications in the catalyst design have been reported for this

* Corresponding author. Fax: +91 33 2473 2805.
E-mail address: msab@iacs.res.in (A. Bhaumik).



Scheme 1. Schematic diagram for the formation of microporous Fe-POP-1, where the curved lines are for the extension of polymerization reaction. Because of the presence of two types of catalytic sites, this polymer showed bi-functional catalytic property in the base catalyzed Knoevenagel condensation and selective oxidation of alcohol to aldehyde and ketone.

reaction, which contains both phase transfer catalyst (PTC) [31], pyridine-functionalized porous polymers [32], DABCO based ionic liquid [33], porous coordination polymer [34], cation-exchanged zeolites [35], primary amine functionalized MCM-41 [36] and so on.

We have synthesized very high surface area microporous organic polymer Fe-POP-1 containing both Fe-free porphyrin and metalloporphyrin building blocks through hydrothermal treatment of pyrrole with terephthalaldehyde in the presence of very small amount of FeCl_3 [37]. Here the porphyrin moieties are repeatedly bridged by phenyl linkers leaving behind entrapped Fe(III) sites within the porous skeleton (Scheme 1). Thus, both basic and Fe(III)-containing sites are present in the material and these can be utilized in bifunctional catalytic reactions [38]. Mimicking the biological pathways with metalloporphyrin based systems for the development of catalytic process have witnessed an exceptional growth over last few decades [39]. Metalloporphyrins, which are supposed to be used as models for cytochrome P-450 enzyme, catalyze several oxidation, alkene epoxidation, alkane hydroxylation and so on [40]. Unlike homogeneous metalloporphyrin based systems, which possess inherent difficulty in separating the catalyst from the reaction mixture together with the cost of the catalyst, supported metalloporphyrin matrices serve advantages like prevention of catalyst from intermolecular self-oxidation, dimerisation of sterically unhindered porphyrins and easy separation from reaction mixture [41,42]. Thus, it is ecologically viable to use the high surface area Fe-POP-1 for selective liquid phase oxidation of alcohols using TBHP as oxidant. In addition remaining basic N-sites of the built-in porphyrin moieties have been employed for the first time as solid phase heterogeneous base catalyst for the Knoevenagel condensation between aromatic aldehyde and malononitrile at room temperature.

2. Experimental

Terephthalaldehyde was purchased from Sigma–Aldrich. Pyrrole was purchased from SRL, India and distilled prior to use. Glacial acetic acid, TBHP and all other organic solvents were procured from Merck, India and were used after purification. Carbon, hydrogen and nitrogen contents of Fe-POP-1 were determined using a Perkin Elmer 2400 Series II CHN analyser. Loading of Fe in Fe-POP-1 was estimated through chemical analysis by using a

Shimadzu AA-6300 double beam atomic absorption spectrometer (AAS). Fourier Transform Infra Red (FTIR) spectra of the samples were recorded using a Nicolet MAGNA-FT IR 750 Spectrometer Series II. Mass spectrometric data were acquired by the electron spray ionization (ESI) technique at 25–70 eV in a Micromass Q-tof-Micro Quadrupole mass spectrophotometer. Nitrogen sorption experiments and micropore analysis were conducted at -195.8°C using Beckman Coulter, SA 3100 instrument. Prior to adsorption measurement the sample was degassed in vacuum at 180°C for about 3 h. NLDFT pore-size distribution of Fe-POP-1 was obtained using the carbon/slit-cylindrical pore model as reference. The ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectrum was recorded on a Bruker Avance III600WB 600 MHz spectrometer at 150.9 MHz and a MAS frequency of 12 kHz. Thermogravimetry (TGA) and differential thermal analyses (DTA) of the samples were carried out in a TGA Instruments thermal analyser TA-SDT Q-600 under nitrogen atmosphere with heating rate $10^\circ/\text{min}$. EPR measurements were performed on a Bruker EMX EPR spectrometer at X-band frequency (9.46 GHz) at liquid nitrogen temperature (77 K). Transmission electron microscopic (TEM) images of the microporous polymer were recorded by using a JEOL JEM 2010 transmission electron microscope operated at 200 kV. The samples were prepared by dropping a colloidal suspension of the sample obtained after sonicating the sample for 2 min with methanol onto the carbon-coated copper grids. UV–visible diffuse reflectance spectra were recorded on a Shimadzu UV 2401PC spectrophotometer fitted with an integrating sphere attachment and using BaSO_4 as background standard. Products of the catalytic reactions were analyzed through the isolated yield and ^1H and ^{13}C NMR analysis. ^1H and ^{13}C NMR experiments (liquid state) were carried out on a Bruker DPX-300 NMR spectrometer.

2.1. Synthesis of Fe-POP-1

In a typical experiment in a flame dried round bottom flask freshly distilled pyrrole (0.025 g, 0.37 mmol) was mixed with terephthalaldehyde (0.05 g, 0.37 mmol). Then 15 ml glacial acetic acid was added into the mixture with constant stirring along with ferric chloride (0.44 mmol) under inert nitrogen atmosphere. The whole solution was stirred in a magnetic stirrer and after 3 h the mixture was transferred to a Teflon lined autoclave and kept under hydrothermal treatment for 72 h at 180°C . After 3 days the autoclave was slowly cooled down to room temperature and a dark brownish product was separated out from the reaction mixture. The precipitated solid was filtered and thoroughly washed with distilled water, methanol, acetone, THF and dichloromethane, respectively, and then vacuum dried in an oven at 80°C for another 48 h. The material was further rigorously washed through Soxhlet extraction for 24 h with water, methanol and tetrahydrofuran (THF), respectively, to give 0.095 g yield of Fe-POP-1. Elemental analysis (%) observed through combustion: C, 77.0; H, 4.3; N, 7.8. Found by EDX analysis (wt%) C, 88.4; N, 2.3. Calcd. Theoretical formula for an infinite unit of Fe-POP-1 is $\{\text{C}_{44}\text{H}_{26}\text{N}_4\}_n$ with C, 86.5; H, 4.2; N, 9.2 and $n = 1 - \infty$.

2.2. Oxidation reaction

For the selective oxidation reaction flame dried round bottom flask was charged with substrate alcohol (1 mmol), Fe-POP-1 (20 mg, 0.00004 mmol Fe(III)), 1.5 mmol TBHP (70 wt% in water) in 5 ml CH_3CN and the resulting mixture was stirred in a magnetic stirrer at 70°C under nitrogen atmosphere. The progress of the reaction was monitored by TLC using ethyl acetate:hexane (6:4) as eluent. After completion of the reaction, the catalyst was simply filtered and washed thoroughly by diethyl ether and then extracted with a mixture of hexane and diethyl ether. The organic fraction was

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