

Mono-functionalization of porous aromatic frameworks to use as compatible heterogeneous catalysts in one-pot cascade reactions

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ARTICLE INFO

Article history:

Received 12 July 2013

Received in revised form 4 September 2013

Accepted 27 September 2013

Available online 6 October 2013

Dedicated to Professor Daniel Brunel on the occasion of his 70th birthday.

Keywords:

Porous polymeric aromatic framework

Post-modification

One-pot

Acid–base catalysts

ABSTRACT

Porous aromatic frameworks (PPAFs) prepared by microwave assisted synthesis can be easily functionalized to obtain solid acid (sulfonic acid) and base (primary amine) catalysts. This porous material demonstrated to be an excellent support of different functional groups. The combination of these functionalized PPAFs was successfully applied as compatible heterogeneous catalysts for cascade reaction of hydrolysis of dimethoxymethylbenzene, acid catalyzed, and Knoevenagel catalyzed by base. The advantages of this catalytic system are its easy synthesis, good catalytic activity, coexistence of incompatible functional groups in homogeneous conditions, with different acid/base ratio, and is recycled up seven times without significant loss of activity. Our concept can be extended to other various one-pot incompatible homogeneous systems and make a contribution toward the creation of environmentally inspired chemical processes through the promotion of multiple reactions in a single reactor.

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1. Introduction

Solid acid and base catalysts have received much attention because of their potential applications for replacing inorganic liquid acids or alkalis in industry [1–3]. The immobilization of soluble catalysts generally in solid supports, such as zeolites [1–4], ordered mesoporous materials (MCM-41 and SBA-15) [1–7] has advantages in comparison with homogeneous counterparts when applied in organic synthesis. The main advantages are that handling and separation of the catalyst from the reaction mixture are easier; catalyst stability is greater and can be recycled to minimize waste production. Most of those soluble catalysts have also been supported on well-structured micro and mesoporous inorganic and organic–inorganic hybrid materials such as MOFs (metal organic frameworks) and PMOs (periodic mesoporous organosilicas). It has been challenging to have new solids as structured purely organic materials (POFs) [8–13,19] with pore dimensions in the micro and mesoporous range, including porous aromatic frameworks (PPAFs) with diamond-like structure [14,15], to be used as catalysts supports due to their high stability, high specific

surface areas and easy functionalization. These porous materials have ultrahigh surface area and high stability making them good candidates to develop potential applications in gas storage [16] and gas separation [8–13] and heterogeneous catalysis [17,20]. Porous aromatic frameworks were previously prepared by thermal conditions starting from *tetrakis*-(4-iodophenyl)methane as a tetrahedral unit and a diboronic acid as a linker [18–20]. Post-synthesis modification of PAFs has been reported to obtain materials for CO₂-uptake [21–24]. Thus, Zhou and co-workers have prepared sulfonated [22] and chloromethyl [23] PPAFs, the latter being further modified to amine groups. Recently, we have reported the first example of bi-functionalized PPAF with acid and base groups (PPAF-SO₃H-NH₂) and demonstrated that groups that cannot coexist in solution can be effectively used in catalytic reactions by immobilizing them in the same structure [25]. For those reactions in which a cooperative effect between the different active centers is not necessary, can be very interesting to apply catalysis with different active centers on separate supports to catalyze one-pot reactions or cascade [26–29]. This paper shows the first approximation to synthesize monofunctionalized-PPAF and the study of catalytic behavior of a mixture of acid- and base-PPAF. The advantages to have the functionality in different physical materials are that we can design new catalysts and combined to get different active catalytic mixtures, i.e. acid PPAF + strong base-PPAF,

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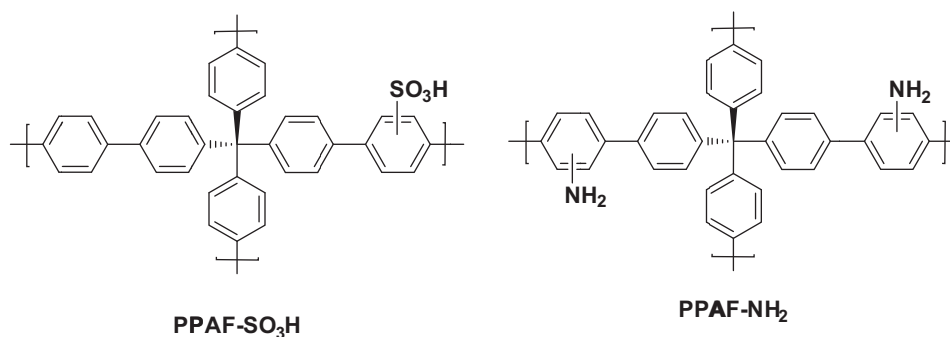


Fig. 1. Structure of PPAF-SO₃H and PPAF-NH₂.

acid+metal-PPAF. In this work, we demonstrate that sulfonic acid- or amino-mono-functionalized porous aromatic frameworks (PPAF-SO₃H and PPAF-NH₂) (Fig. 1) can be also applied as mixture of catalysts for a two steps one pot cascade reactions. Moreover, the solid mixture consisting of the PPAF-SO₃H + PPAF-NH₂ catalysts was easily recovered by simple filtration and then could be reused at least seven times with retention of high catalytic activity and selectivity.

The novel catalysts were prepared by post-functionalization of the starting support PPAF-1. This support was prepared from *tetrakis*-(4-bromo or 4-iodo)phenylmethane as building block (Scheme 1) instead of the previously reported 2,2',7,7'-tetrabromo or tetraiodo 9,9'-spiro-bisfluorene [25], to facilitate the formation of a more ordered network.

2. Experimental

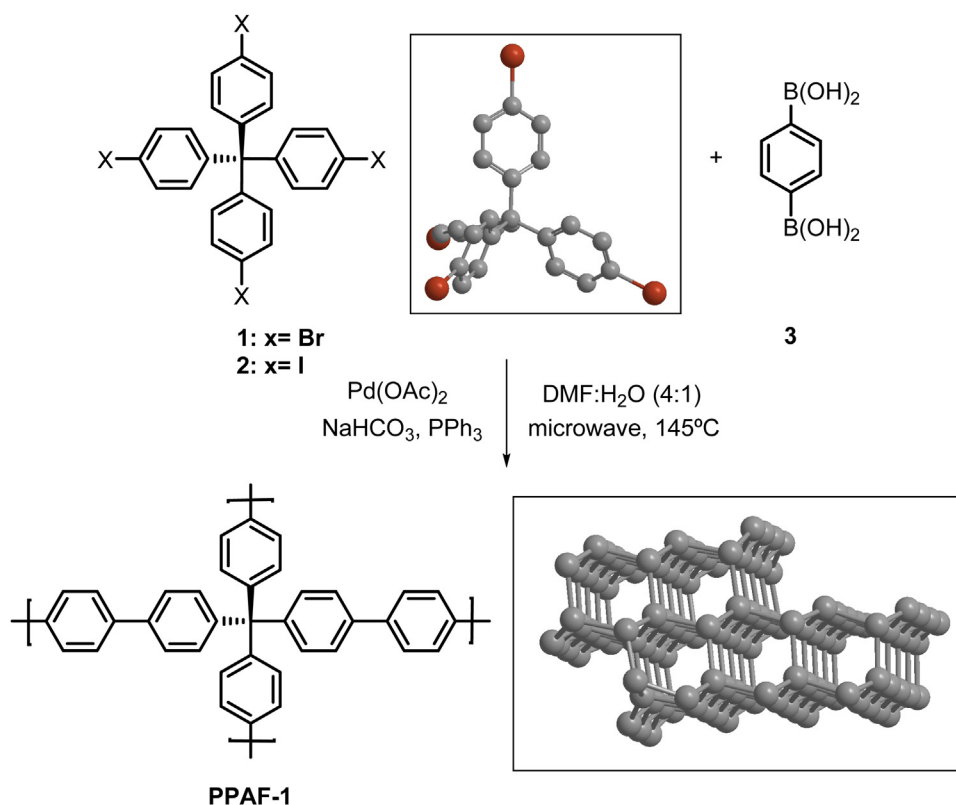
All starting materials were purchased from commercial suppliers and used without further purification unless

otherwise noted. *Tetrakis*-(4-bromophenyl)methane **1** and *tetrakis*-(4-iodophenyl)methane **2** were prepared according to a previously reported method [30,31]. All reactions were performed under a purified nitrogen atmosphere. %C, %N, %S and %H contents were determined in a LECO CHNS-932 analyzer. Thermogravimetric and differential thermal analyses (TGA-DTA) were conducted in an air stream with a TA-Q500 instrumental analyzer. The samples were heated under an air stream from 40 to 850 °C with a heating rate of 10 °C/min.

IR spectra were recorded on a Perkin Elmer Spectrum One spectrometer and are reported in terms of frequency of absorption (cm⁻¹).

¹³C solid-state MAS-NMR measurement was recorded with a Bruker AV400 WB spectrometer (Larmor frequencies of 400 and 100 MHz, using 4 mm MAS probes spinning at 10 kHz rate).

Nitrogen adsorption isotherms were measured at 77 K using a Micromeritics ASAP 2020. Prior to measurement, the samples were degassed for 12 h at 200 °C. The pore size average was determined either by BJH method.



Scheme 1. Synthesis of PPAF-1 support.

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