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Acid and base coexisted heterogeneous catalysts supported on hypercrosslinked polymers for one-pot cascade reactions

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ABSTRACT

Heterogeneous microporous acid (sulfonic acid) and base (benzylamine) catalysts with high surface areas were synthesized using simple aromatic compounds through one-step external cross-linking reaction. The direct induction and control of catalytic sites were achieved by functionalized monomers using an appropriate amount of acid/base monomers. This strategy provides an easy approach to produce highly stable and acid/base functionalized microporous organic polymers. The structure and composition of the catalysts were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen sorption, Fourier transform infrared spectroscopy (FT-IR), solid-state ^{13}C cross polarization magic angle spinning (CP/MAS) NMR, thermogravimetric analysis (TGA), and element mapping analysis. The stable porous skeleton and the accurate manipulation of the catalyst structure allowed us to use the obtained polymers as compatible and efficient acid/base co-catalysts for one-pot cascade reactions. We demonstrated the use of these microporous heterogeneous catalysts for the cascade deacetalization/Henry and deacetalization/Knoevenagel reactions. The results demonstrated that preparing microporous materials from simple aromatic compounds through one-step external cross-linking reaction is indeed a cost-effective and easy-to-handle method to produce functionalized heterogeneous catalysts. The microporous heterogeneous catalysts produced by this method are highly stable and the amount of catalytically active sites can easily be controlled to form a catalytic system with two antagonistic centers.

1. Introduction

Heterogeneous catalysts are preferred over homogeneous systems for industrial processes because of their easier separation and recycling ability [1–4]. Multistep organic reactions generally require different catalysts in various steps, sometimes even cooperating catalysts with antagonistic groups. For the continuous reactions, various attempts have been made to develop heterogeneous catalysts by simulating enzymes, which have both acidic and basic groups in one molecule and can efficiently catalyze tandem processes to produce various biomolecules to improve the overall reaction efficiency by omitting the separation of catalyst from the product [5–7]. For this purpose, many heterogeneous catalysts containing acidic and basic groups immobilized on a carrier have been designed, including inorganic-supported catalyst [8–11], organic-inorganic hybrid catalyst [12–15], and organic-supported catalyst [16–18]. However, some issues are accompanied, including low catalytic activity due to weak acidity caused by an unavoidable neutralization between acid and base sites in the preparing process [10,19], complicated protection and de-protection operations [16,20], and easy deactivation of basic sites resulted from strong acid treatment during the base de-protection process [8,9], all which hampered the researchers to manipulate the loading and catalytic strength of the active sites. To overcome these shortcomings, few mono-functionalized catalysts in which acid and base groups located on different supports have also been employed [17,18]. With this method, it is usually easier to achieve an adjustable combination of acidic and basic catalytic sites by adding the acid and base components separately. However, to maximize the efficiency of this method for cascade reactions, following issues need to be addressed while designing an acid-base co-catalyst system: (i) generation of acidic and basic catalytic sites on two separate supports having the similar chemical/physical properties as much as possible *i.e.*, lipophilicity and

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porosity rather than on different materials to minimize the mass transfer issues of reactants and intermediates in liquid phase reactions; (ii) because of the presence of antagonistic species, the supporting material and also the linkers between the catalyst and the support should have excellent thermal and chemical stability; otherwise, leaching of one type of catalyst into the reaction solution will poison another, resulting in rapid deactivation of the catalyst; (iii) to facilitate the manipulation of the reaction selectivity, the loading of acidic and basic groups and also their strengths should be controlled precisely. All these factors put together tend to support the necessity of the development of a suitable method to prepare acid and base catalysts for establishing a site-isolated co-catalyst system, which we have now achieved.

Microporous organic polymers (MOPs), as an important class of microporous materials, have recently emerged as versatile platforms for the development of catalysts because of their unique properties, including superior chemical and thermal stabilities, high surface area, and low skeleton density [21–25]. Hypercrosslinked polymers (HCPs), a type of MOPs, possess not only the merits of MOPs but also distinct features of low-cost and facile preparation, monomer diversity, and tunable pore size [25–27]. The attainment of permanent porosity in HCPs, which is critical to high efficiency of catalyst, is done by sufficient chemical crosslinkage that prevents the polymer chains from collapsing into a dense, nonporous state [28,29]. We recently have reported a series of cost-effective HCPs-type catalysts using the “knitting” strategy in some organic transformations, which testify that HCP material is a promising catalyst or support for organic catalysis [28,30,31].

Herein, we report a strategy for preparing monofunctionalized acid and base catalyst (HCP–SO_3H and HCP–CH_2NH_2), in which the catalytic sites are well-distributed in the backbone of the microporous polymer (Fig. 1a). The acid and base groups were induced directly by the monomer, and their loading can also be controlled precisely. Because the synthesis of catalysts is accomplished in only one step, this new synthetic protocol is cost-effective with readily available starting materials and simple to operate. Interestingly, because the acid and base groups are located in the backbone of the polymer matrix, the obtained acid- or base-functionalized microporous materials are highly stable. Therefore, these catalysts are capable of catalyzing the following one-pot tandem reactions: deacetalization-Henry reaction (Fig. 1b) and deacetalization-Knoevenagel reaction, both which require the acid-base co-catalyst to synthesize many useful pharmaceutical intermediates [32,33] and important organic synthesis intermediates [34,35]. In the selected reactions, the catalysts display good activity and selectivity, and are easily recovered and reused several times without significant loss of activity.

2. Results and discussion

The HCPs–SO_3H catalyst obtained with different ratios of benzene to sodium 4-(phenylamino)benzenesulfonate is labeled as HCPs–SO_3H–X, where X refers to the mole fraction of sodium 4-(phenylamino)benzenesulfonate in the substrates. Similarly, the HCPs–CH_2NH_2 obtained with different ratios of benzene and benzylamine are labeled as HCPs–CH_2NH_2–X, where X refers to the mole fraction of benzylamine in the substrates (substrates refer to benzene and acid or base precursor).

The FT-IR spectra of HCPs–SO_3H–50 and HCPs–CH_2NH_2–50 are shown in Fig. 2. Comparing with the homogeneous counterpart 4 -(phenylamino)benzenesulfonate, the weak C–H stretching absorption of aromatic rings at 3000–3100 cm^{-1} in HCPs–SO_3H–50 is absent, while the characteristic peak of benzene skeleton stretching in the 1450–1600 cm^{-1} region is visible. In addition, the characteristic absorption peaks of sulfonic acid group at 1382 cm^{-1}, 1198 cm^{-1}, 1037 cm^{-1}, and 805 cm^{-1}, which are due to asymmetrical and symmetrical stretching vibrations of S–O, are retained in HCPs–SO_3H–50 [36,37]. A weak peak at 1091 cm^{-1} can be assigned to C(aromatic)–S stretching vibration showing the presence of sulfonic acid in the HCPs–SO_3H polymer. Moreover, a broad and a strong band ranging from 3100 to 3650 cm^{-1} in HCPs–SO_3H may be associated with the –OH stretching vibration. These results indicate that the target HCPs–SO_3H–50 catalyst was obtained through the hyper-crosslinking reaction. In the FTIR spectra of HCPs–CH_2NH_2, the absorptions at 2917 cm^{-1} and 2903 cm^{-1} are clearly visible and account for the –CH_2–

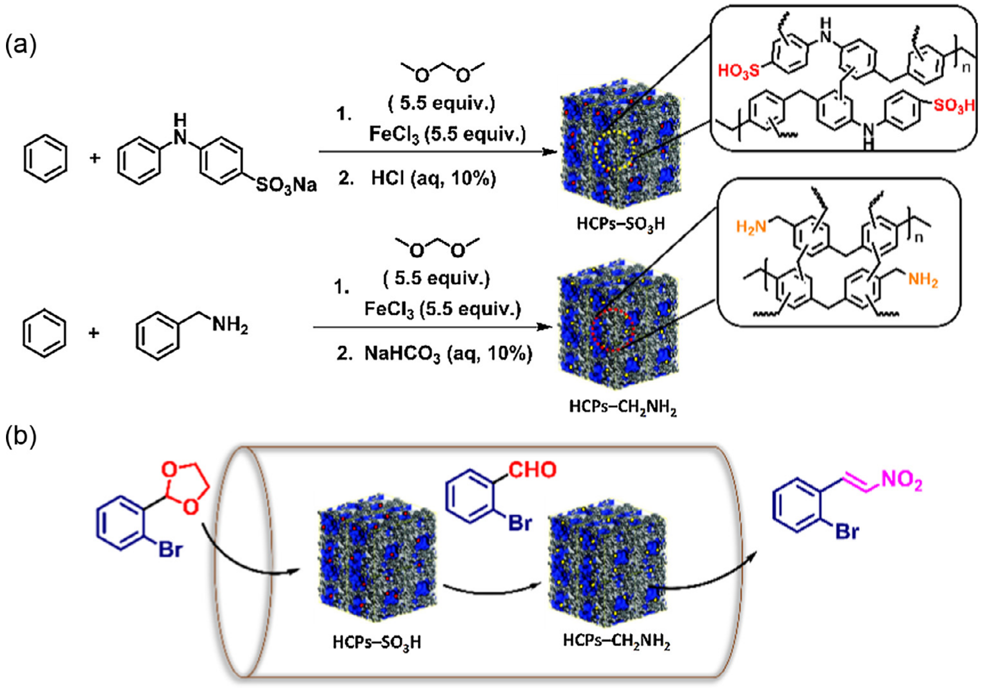

Fig. 1. Schematic illustration for (a) the fabrication of HCP–SO_3H and HCP–CH_2NH_2 and (b) the one-pot cascade reaction.