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Dual-functionalized porous organic polymer as reusable catalyst for one-pot cascade C—C bond-forming reactions

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ABSTRACT

A porous dual-functional acid-base covalent organic polymer catalyst (CBAP-1(EDA-SO_3H)) was prepared using a facile Friedel-Crafts reaction of triphenylbenzene and terephthaloyl chloride to prepare the polymer backbone (CBAP-1) followed by functionalization with ethylenediamine (EDA) and a simple chlorosulfonic acid treatment. The resultant polymeric catalyst and its functional moieties were characterized by Fourier transform infrared (FTIR), elemental analysis (EA), X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), and N_2 adsorption-desorption isotherm analyses. The catalytic activity of CBAP-1(EDA-SO_3H) was then assessed for one-pot cascade C—C bond-forming reactions involving deacetylation-Knoevenagel condensation and Henry reactions. Compared with the homogeneous catalyst and CBAP-1 functionalized with just acid or base, CBAP-1(EDA-SO_3H) showed superior catalytic activity and selectivity, and was found to be reusable for up to seven consecutive runs. A catalytic mechanism for C—C bond-forming reactions over CBAP-1(EDA-SO_3H) was proposed.

1. Introduction

Efficient and sustainable catalytic processes that minimize the production of environmentally polluting byproducts by achieving high selectivity in short reaction times are highly desirable for the chemical industry. In this regard, synergistic catalysis in one-pot cascade reactions from simple substrate molecules is important because it is a more efficient, atom economical, time saving, and environmentally friendly strategy for the synthesis of complex organic compounds than traditional stepwise reactions [1–3]. The synergistic reaction strategy utilizes catalysts with two or more active sites in close proximity to activate the reactants, reducing the activation energy barrier, number of reaction steps, necessity for purification of the intermediates, need for multi-solvents, and energy consumption [4,5]. These reactions are catalyzed by the intial active sites on the catalyst to produce the intermediates, which are then further activated by adjacent catalytic sites to form the final products [6]. This type of synergistic catalysis has become increasingly employed in nanocatalysis [7,8], enzyme catalysis [9], electrocatalysis [10], and photocatalysis [11], all of which present opportunities for cascade organic reactions [12–14].

Many homogeneous catalysts are applied to cascade reactions requiring dual acid-base functionality [15–18]. However, homogeneous catalytic systems have well-known problems in regarding product separation and reusability, increasing costs and environmental impact [15,17,18]. In addition, bifunctional acid-base catalytic activity is easily deactivated in homogeneous reaction media owing to acid-base neutralization. Therefore, solid heterogeneous bifunctional acid-base catalysts in which the acidic and basic functional groups are fixed in different locations in the solid matrix have received increasing attention for one-pot cascade reactions [19–22]. To date, cooperative bifunctional acid-base bifunctional catalytic sites on silica [23,24], heteropoly acids [25], metal organic frameworks [26–28], metal oxides [29], graphene oxide [30], and covalent organic polymers [19] have been employed for cascade reactions. For example, Shylexh et al. reported the use of bifunctional acid-base periodic mesoporous organosilica for deacetylation-Knoevenagel reactions [23]. Among other examples, Shiju et al. developed phosphotungstic acid immobilized mesoporous silica for deacetylation-Henry reactions [25], amine-functionalized MIL-101(Al)-NH_2 has been used for deacetylation-Knoevenagel reactions [28], Li et al. prepared Mg-Al oxide-incorporated Al-containing mesoporous silica for one-pot cascade deacetylation-Knoevenagel reactions [29], and Zhang et al. synthesized an amine-functionalized graphene oxide catalyst for deacetylation-Knoevenagel reactions

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[30]. Recently, Shinde et al. have synthesized a porphyrin-based covalent organic framework using dihydroxyterephthalic acid and 5,10,15,20-tetrakis(4-aminophenyl)porphyrin molecules for the deacetylation-Knoevenagel reaction, in which the amino-porphyrin connection was formed by a two-step reaction [19]. However, in these studies, it was often necessary to employ a protection-deprotection procedure to avoid acid-base neutralization. In addition, multi-step syntheses were necessary to synthesize the solid support materials. Therefore, the development of low-cost, simple syntheses of heterogeneous solid catalysts incorporating stable acid-base functional moieties for acid-base one-pot cascade reactions is highly desirable.

Recently, porous covalent organic polymers have drawn increasing interest as heterogeneous catalysts owing to their tunable chemical functionalities, high surface areas, and high chemical stabilities in different reaction media. High surface area and tunable chemical functionality is advantageous for enhanced adsorption and activation of reactants [31–33]. In addition, the high chemical stability of the support material should help avoid the contamination of the products [34,35]. Recently, highly porous covalent organic polymers containing carbonyl units that were modified with different amine compounds were prepared via a facile Friedel-Crafts reaction using readily available commercial chemicals [36,37]. Herein, we applied this strategy to the preparation of an efficient dual-functional acid-base covalent organic polymer catalyst. The developed catalyst was successfully applied to two-step one-pot cascade C—C bond-forming reactions that involved acid-catalyzed deacetylation followed by base-catalyzed Knoevenagel and Henry reactions. Recycling studies were also conducted to demonstrate the high stability of the catalyst.

2. Experimental section

2.1. Materials

Anhydrous aluminum chloride, terephthaloyl chloride, 1,3,5-triphenylbenzene, dichloromethane (DCM), ethylenediamine (EDA), sodium borohydride, chlorosulfonic acid, benzaldehyde dimethyl acetal, nitromethane, malononitrile, methanol, and toluene were purchased from Sigma-Aldrich and were used as received without further purification.

2.2. Catalyst preparation

The preparation of the parent porous covalent organic polymer CBAP-1 and post-functionalization with EDA (CBAP-1(EDA)) were conducted according to our previously reported procedure [36]. Briefly, 1,3,5-triphenylbenzene (10 mmol, 3.06 g), terephthaloyl chloride (15 mmol, 3.05 g), anhydrous $AlCl_3$ (15 mmol, 2.00 g), and DCM (180 mL) were mixed in a 250-mL round-bottom flask fitted with a condenser. The reaction mixture was refluxed for 12 h to produce a dark brown solid powder and the precipitated material was filtered and successively washed with DCM, methanol, and water. The product was further purified in a Soxhlet extractor for 10 h using water to completely remove the catalyst and dried under vacuum at 130 °C for 12 h to achieve solvent free CBAP-1 in 92% yield. The C and H contents of CBAP-1 (84.93% C and 4.06% H) from EA (EA, EA1112, Italy) were in good agreement with the theoretical composition (86.21% C and 4.22% H).

The fresh CBAP-1 (1.00 g) was added to an EDA solution (2 mL in 40 mL methanol) and refluxed for 15 h. After cooling to room temperature, $NaBH_4$ (ca. 2.00 g) was added slowly and the mixture was stirred at room temperature for 10 h. Then, the solid mixture was filtered and washed successively with methanol and water, and dried at 130 °C to yield 1.18 g of CBAP-1(EDA).

Then, 1.00 g of CBAP-1(EDA) was placed in 40 mL of dry DCM and cooled to 5 °C in an ice-bath with stirring for 10 min. Chlorosulfonic acid (0.10 mL) dissolved in 5 mL of DCM was then added dropwise into the CBAP-1(EDA) suspension over 5 min, and the resulting mixture was stirred for 2 h at room temperature. Then, the mixture was poured into ice-cooled water (200 mL) and the solid phase was filtered, washed with distilled water (100 mL × 3), and dried at 110 °C to yield 1.04 g of CBAP-1(EDA-SO_3H).

For comparison, CBAP-1(SO_3H) was prepared by the following similar procedure: CBAP-1 (1.00 g) in 40 mL of dry DCM was cooled to 5 °C in an ice-bath with stirring for 10 min. Then, 25 mL of chlorosulfonic acid dissolved in 40 mL of DCM was added dropwise to the CBAP-1 suspension over 1 h, and the resulting mixture was stirred for 3 days at room temperature. The mixture was then poured into ice-cooled water (500 mL) and the solid catalyst was filtered, washed with distilled water (500 mL × 3), and dried at 110 °C to yield 1.03 g of CBAP-1(SO_3H)

2.3. Catalysts characterization

Fourier-transform infrared (FT-IR) spectra of the developed solid catalysts were recorded on a VERTEX 80 V FT-IR spectrometer (Bruker, Germany) using the standard KBr pellet method. Powder X-ray diffraction (XRD) was performed on a Rigaku diffractometer with Cu Kα radiation over $2\theta = 10–60°$ at a scan rate of 2°/min. The surface electronic states were examined using X-ray photoelectron spectroscopy (XPS) with a monochromatic Al Kα X-ray source and a hemispherical analyzer (Thermo Scientific, USA). The textural properties of the solid catalysts were determined from nitrogen adsorption-desorption isotherms, which were recorded at 77 K on a BELsorp-max analyzer (BEL, Japan) after activation of the sold catalyst at 120 °C overnight. The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation in the relative pressure range 0.05–0.10.

2.4. Catalytic reactions

2.4.1. One-pot deacetylation-Knoevenagel reaction

In a typical reaction, benzaldehyde dimethyl acetal (4 mmol), malononitrile (4.2 mmol), CBAP-1(EDA-SO_3H) (80 mg), toluene (4 mL), and H_2O (1 mL) were mixed in a reaction tube fitted with a condenser. The reaction mixture was kept at 70 °C under magnetic stirring for 80 min and aliquots of the sample mixture were extracted using a filter syringe and analyzed on a gas chromatographer equipped with an HP-5 capillary column (Agilent Technologies 7890A, flame ionization detector) to determine the yield of benzalmalononitrile.

2.4.2. One-pot deacetylation-Henry reaction

In a typical reaction, benzaldehyde dimethyl acetal (4 mmol), CBAP-1(EDA-SO_3H) (120 mg), nitromethane (4 mL), and H_2O (1 mL) were mixed in a reaction tube fitted with a condenser. The reaction mixture was kept at 80 °C under magnetic stirring for 7 h and aliquots of the reaction mixture were extracted using a filter syringe and analyzed on a gas chromatographer equipped with an HP-5 capillary column to determine the yield of trans-β-nitrostyrene.

3. Results and discussion

3.1. Catalyst characterization

The dual-functional acid-base catalyst was synthesized by the sequence illustrated in Scheme 1. First, CBAP-1 was synthesized via the Friedel-Crafts reaction of triphenylbenzene and terephthaloyl chloride, followed by functionalization with ethylenediamine to