

Short communication

Ultra-high concentrations of amino group functionalized nanoporous polymeric solid bases: Preparation, characterization and catalytic applications



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ABSTRACT

We report here that the amino-group functionalized nanoporous polydivinylbenzene (PDVB-2.0-NH₂, PDVB-NH₂), acts as an efficient solid base for catalyzing Knoevenagel condensation, which could be synthesized from nitration of nanoporous polydivinylbenzene (PDVB), reduction in the mixture containing SnCl₂ and HCl, and activated with isopropylamine. The resultant solid bases of PDVB-2.0-NH₂ and PDVB-NH₂ have large BET surface areas, abundant nanopores, controlled hydrophobic network and ultra-high concentrations of the amino group. The above characteristics result in their excellent activities and good recyclability for catalyzing Knoevenagel condensation of various aldehydes with malononitrile, much better than those of commercially basic resin of Amberlite-400 and Amberlite-910, which was as comparable as that of the homogeneously strong base of CaO. This work develops efficient nanoporous polymeric solid bases with controllable surface characteristics and ultra high concentrations of basic sites.

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1. Introduction

Acid and base catalytic processes showed an inseparable relationship in the area of catalytic chemistry. In acid catalyzed reactions, reactants act as bases toward catalysts which act as acids. On the contrary, reactants act as acids toward catalysts in base catalyzed reactions [1], and acid and base catalyzed reactions have been paid much attention because of their wide applications for catalyzing production of various useful chemicals [1–11]. Compared with acid catalysis, base catalysis usually exhibits mild reaction conditions and high efficiency [6]. Typical base catalyzed reactions such as aldolization, alkylation, Knoevenagel, transesterification, glucose isomerization Michael condensations, and Wadsworth–Emmons additions are very efficient tools for the fabrication of various fine chemicals and biofuels in the industry [12,13]. Conventional base catalysts such as KOH, NaOH and CaO showed low cost, strong base strength, and excellent activities in various reactions,

however, the drawbacks such as environmental concerns and difficult regeneration from reaction media largely constrain their wide applications [1].

In recent times, the replacement of homogeneous bases with solid bases for catalyzing production of fine chemicals and biofuels has received considerable attention [6,14–16]. Up to now, the common solid bases include alkaline earth oxides, basic zeolites, strong basic resins, clay minerals and hydrotalcite, which have been widely used in various base catalytic reactions, and showed relatively good catalytic activities [1,6,12,17]. However, their relatively low BET surface areas result in the low exposition degree of catalytically active sites and diffusion limitation of reactants in various reactions, which constrains their catalytic activities and lives [1,11,18–20]. Loading the basic active sites into highly porous supports such as zeolites, mesoporous silicas and porous carbons basically overcomes the poor porosity problems of conventional solid bases, and the resultant porous solid bases were active in various base catalyzed reactions such as Knoevenagel reactions, toward transesterification to biodiesel, and Michael addition etc. [1,15,21–24]. However, the reported porous solid bases showed the drawbacks including: (i) the limited contents of basic sites could be loaded into these porous materials and (ii) their sensitive basic sites could be easily poisoned by molecules such as H₂O and CO₂ because of their unique

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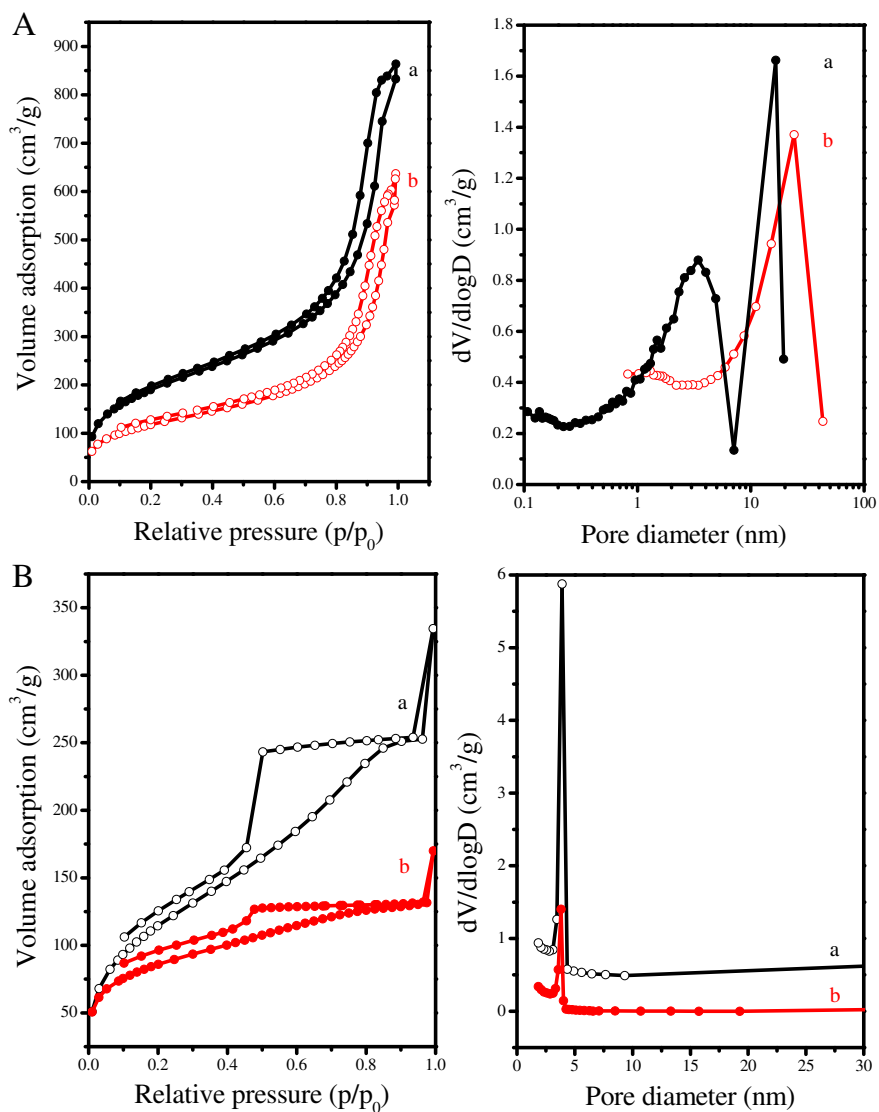


Fig. 1. N₂ isotherms and pore size distribution of (A) PDVB-2.0 and PDVB-2.0-NH₂, and (B) PDVB and PDVB-NH₂.

hydrophilic frameworks. The above problems found in reported solid bases strongly constrain their wide applications in various base-catalyzed reactions [1,6,25,26].

Up to now, it is still challengeable to synthesize porous solid bases with very high concentrations of basic sites and controllable hydrophobicity, which will be very important for the enhancement of catalytic activities and recyclability of solid base catalysts. Recently, our group

successfully synthesized pyridine, imidazole and triazole functional, nanoporous polymeric solid bases, which showed very good hydrophobicity and controlled wettability for various organic reactants. These characters result in their very good stability in the air and good catalytic activity in various reactions [6,17]. However, the limited contents of basic sites that still constrain them are used as highly efficient solid bases in various reactions.

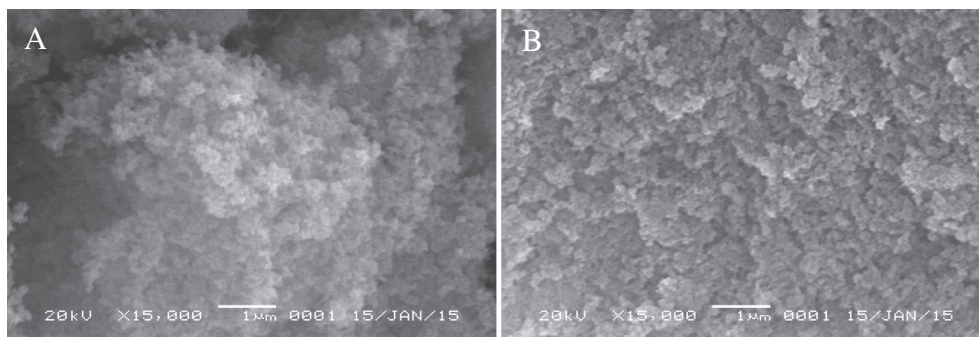


Fig. 2. SEM images of (A) PDVB-2.0-NH₂ and (B) PDVB-NH₂.

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