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Microporous carbon nitride as an effective solid base catalyst for Knoevenagel condensation reactions

Jie Xu*, Kang Shen, Bing Xue, Yong-Xin Li*

Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, College of Chemistry and Chemical Engineering, Changzhou University, Gehu Road 1, Changzhou, Jiangsu 213164, PR China

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ABSTRACT

Microporous graphitic carbon nitride (CN-Mic) material has been prepared using carbon tetrachloride and ethylene diamine as precursors, and a siliceous microporous MCM-22 as a hard template. A series of Knoevenagel condensation reactions have been performed over the CN-Mic sample, and the influences of reaction conditions on the corresponding catalytic behavior have been investigated. The results showed that the CN-Mic material exhibited high catalytic activity and versatility for the condensation reactions. XPS and FT-IR analysis reveal a high abundance of the N-containing groups located on the surface of CN-Mic, which accounts for the superior catalytic activity of the carbon nitride material as a promising new type of heterogeneous Lewis base catalyst for the condensation reactions. It is also revealed that the activity of CN-Mic is much higher than those obtained over mesoporous g-CN materials. Meanwhile, the catalytic results of CN-Mic compared favorably with those of other g-CN materials for Knoevenagel reactions reported previously. In addition, a mechanism for the CN-Mic catalyzed Knoevenagel condensation was tentatively proposed.

1. Introduction

Knoevenagel condensation (the reaction between an aldehyde and an active methylene-containing reagent) is one of the most primary processes to synthesize valuable α,β-unsaturated carbonyl compounds that are widely utilized in the pharmaceutical industry [1,2]. Conventionally, Knoevenagel condensation reactions proceed homogenously in the presence of various base catalysts [3], which can activate the methylene-containing reagent by abstracting an acidic proton from it. These catalysts are mainly nitrogen-containing molecules such as aliphatic amines, urea and piperidine or their corresponding ammonium salts and amino acids [4]. Notwithstanding their high catalytic activity, the thorny issues associated with the separation and recycling of the catalyst cannot meet the increasing demand on green and sustainable catalysis nowadays. Several heterogeneous inorganic salts, such as phosphates and halides, have also been reported as catalysts in the Knoevenagel condensation. However, the use of such materials leads to metal contamination of the products [5]. Recently, ionic liquid or organic amine immobilized mesoporous silica materials have been extensively used as base catalysts [6]. Nevertheless, the drawback of limited number of active sites along with easy leaching of anchored catalysts restrains a further catalytic application of these materials. Owing to the increasing attention toward the development of green and sustainable heterogeneous catalysis, it is imperative to search a more efficient and sustainable catalyst for Knoevenagel condensation process.

As one of the most appealing and promising metal-free materials, graphitic carbon nitride (g-CN) has recently received a great deal of attention in many research fields [7,8]. The success of g-CN is largely attributed to its unique combination of various physicochemical properties. Of particular note is that the incorporation of N atoms into the C nanostructures endows g-CN with plenty of basic sites in the forms of amine groups, etc. [9], which dictates an intrinsically basic function. Hence, the exploitation of g-CN has opened new and exciting opportunities in the fields of base catalysis. Park et al. [5] reported mesoporous g-CN as metal-free base catalyst for Knoevenagel condensation reactions, wherein g-CN materials exhibited efficiently catalytic activity under microwave irradiation, affording high yields of 75–95% within short time of 12 min. Wang et al. [10] reported the synthesis of high-surface-area g-CN using cyanamide as precursor. After the pretreatment of deprotonation by tBuOK or KOH solution, the g-CN materials demonstrated higher catalytic activity for various Knoevenagel condensation as well as transesterification reactions.

Although the results above have evidenced the catalytic potential of g-CN materials in Knoevenagel condensation reactions and other organocatalysis processes, it should be mentioned that the high catalytic results were achieved under an assisted condition or pretreatment, i.e. microwave irradiation or deprotonation. In fact,

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* Corresponding authors. Tel.: +86 519 86330135.
E-mail addresses: shine6832@163.com (J. Xu), liyxluck@126.com (Y.-X. Li).

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poor catalytic yields were obtained if using bare g-CN materials without any promoting condition. From both practical and sustainable points of view, it is highly desired to develop a readily usable and effective g-CN catalyst capable of facilitating Knoevenagel condensation under mild conditions.

Herein, we employ microporous g-CN material (CN-Mic) as a catalyst for a series of Knoevenagel condensation. The catalytic results have revealed that CN-Mic can be used readily without any assisted reaction condition or catalyst pretreatment, and exhibited high efficiency for the condensation between various aldehydes and methylene group-containing compounds. Furthermore, the catalytic performance of CN-Mic has been compared in detail with those obtained over other g-CN materials reported previously. In addition, a possible mechanism for the CN-Mic catalyzed Knoevenagel condensation has been proposed.

2. Experimental

2.1. Catalyst preparation

CN-Mic sample was prepared according to the established templating-assisted method [11]. In a typical procedure, 2.0 g of MCM-22 powder was added into the previously well-mixed solution containing 6.0 g of carbon tetrachloride (CTC) and 3.6 g of ethylenediamine (EDA). The mixture above was then heated at 90 °C for 6 h under refluxing to induce polymerization of the precursors, followed by drying at 50 °C overnight. The obtained dark-brown solid was heated from room temperature to 600 °C at a ramp of 3 °C min^{-1} and kept in 600 °C for another 5 h under argon atmosphere. Finally, the CN-Mic sample was recovered after washing with NH_4HF_2 aqueous solution (4 mol L^{-1}) to remove the template. The yield of resultant sample was around 0.7 g.

2.2. Samples characterization

Structural analysis of MCM-22 and CN-Mic samples was carried out on a Bruker D8 Advance X-ray diffractometer (XRD) equipped with a graphite monochromator, operating at 40 kV and 40 mA and employing nickel-filtered Cu Kα radiation ($\lambda = 1.5418$ Å).

Nitrogen adsorption at −196 °C was measured using a Micromeritics ASAP 2020 after the samples were degassed (1.33×10^{-2} Pa) at 150 °C for 4 h. The specific surface area (S_{BET}) was calculated using the Brunauer–Emmett–Teller (BET) method. The pore diameter and pore size distribution were determined from the Horvath–Kawazoe (H–K) method.

The X-ray photoelectron spectra (XPS) of the CN-Mic sample was measured using a Perkin-Elmer PHI 5000C spectrometer working in the constant analyzer energy mode with Mg Kα radiation as the excitation source. The carbonaceous C 1*s* line (284.6 eV) was used as the reference to calibrate the binding energies (BE).

FT-IR spectrum of the sample was collected on a Bruker Tensor spectrometer via the usual KBr pellet technique. Elementary analysis (EA) was performed with EA2400 II (PerkinElmer) instrument to determine the carbon, nitrogen, hydrogen, and sulfur content of the sample.

2.3. Catalytic test

Catalytic tests for Knoevenagel condensation reaction were carried in a two-neck round bottomed flask (25 mL). 10 mmol of aldehyde, 10 mmol of methylene group-containing nitrile, 0.5 mL of *n*-decane as internal standard, and 5 mL of solvent (CH_3CN or *n*-butanol as desired) were mixed well. 100 mg of CN-Mic sample was added into the mixture and the catalytic tests were performed at 90 °C for 4 h. After the reaction, the mixture was centrifuged and analyzed by GC–MS. The filtered catalyst was washed with ethanol for two times, dried overnight, and then investigated for its next running.

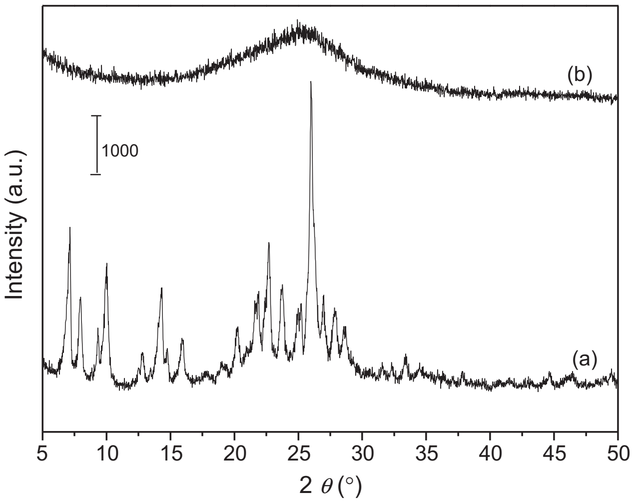

Fig. 1. XRD patterns of MCM-22 (a) and CN-Mic (b) samples.

3. Results and discussions

3.1. Catalyst characterization

The powder XRD patterns of the microporous CN-Mic material together with the parent zeolite template (MCM-22) are shown in Fig. 1. In sharp contrast with the template, which exhibits a highly intense diffraction peaks, the CN-Mic sample prepared via nanocasting method demonstrates broad and weak diffraction peaks. The peak located at $2\theta = 25.5°$ corresponding to the (0 0 2) diffraction (interlayer of the graphitic sheets) with a *d* spacing of 3.50 Å is similar to the *d* spacing obtained in the bulk carbon nitride ($d = 3.36$ Å) materials reported previously [11,9]. This indicates the formation of turbostratic ordering of carbon and nitrogen atoms in the CN graphene layers of CN-Mic [12].

Fig. 2 shows the N_2 adsorption isotherms and the corresponding pore distribution of the parent MCM-22 sieve and CN-Mic sample.

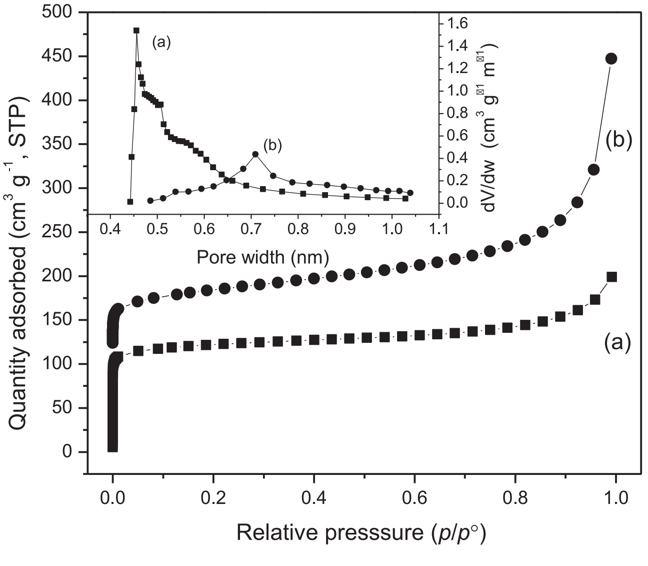

Fig. 2. N_2 adsorption isotherms of MCM-22 (a) and CN-Mic (b) samples. The insert shows the corresponding pore distribution of the samples.