



Short communication

Trace water/amino-modified silica aerogel catalytic system in the one-pot sequential reaction of benzaldehyde dimethyl acetal and nitromethane



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ARTICLE INFO

Article history:

Received 4 August 2016

Received in revised form 4 November 2016

Accepted 29 November 2016

Available online 01 December 2016

Keywords:

Synergistic catalysis

Porous material

One-pot reaction

Silica aerogel

ABSTRACT

In this work, we demonstrate that solid-base such as amino-modified silica aerogel (SA-NH₂) together with trace water showed excellent catalytic performance in one-pot sequential reaction of acid-catalyzed benzaldehyde dimethyl acetal hydrolysis and base-catalyzed Henry reaction which was usually catalyzed by acid-base bifunctional heterogeneous catalyst. The role of trace water in the reaction was discussed by batch control experiment. This SA-NH₂/water catalytic system showed high reactant conversions (>99%) and main product selectivities (up to 99.4%). The trace water induced acid catalysis mechanism and a possible H⁺/-NH₂ coexistence mechanism were given to explain the synergistic catalytic effect of solid-base and trace water.

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1. Introduction

One-pot cascade reactions, which contain two or more chemical steps and therefore reduce the synthesis steps such as intermediate isolation and purification, save energy consumption, lower operation cost, and decrease the amount of waste, have attracted increasing attention in recent years [1–6].

Trans-1-nitro-2-phenylethylene, which is an important chemical intermediates for slimicides and dyes, is prepared from benzaldehyde and nitromethane. However, benzaldehyde is not stable for storage and transportation and usually stored in the form of benzaldehyde dimethyl acetal. Thus the synthesis of trans-1-nitro-2-phenylethylene needs two steps: (1) acid-catalyzed benzaldehyde dimethyl acetal hydrolysis to obtain benzaldehyde and (2) base-catalyzed Henry reaction of benzaldehyde and nitromethane to obtain the target product trans-1-nitro-2-phenylethylene [7–8]. In recent years, various acid-base bifunctional heterogeneous catalysts containing isolated acidic and basic groups have been developed to realize this two-step sequential reaction in a single reactor [2,7–12]. These catalysts were usually prepared by anchoring acidic groups [13–18] (such as —COOH, —SO₃H, —SH) and basic groups [13–23] (such as NH₂, —NRH, —NR₂) or amino acids [24–25] (lysine and proline) with both the acidic and basic sites on porous substrates, long-chained polymers or metal-organic frameworks. However, the preparation process for most of the catalysts is tedious, including grafting of organic groups, protecting acid or base precursors,

and generating acid or base catalysts [2,10]. Therefore, developing new facile catalytic system for this special reaction is essential for their industrial application.

In this work, we demonstrate that trace water together with the easy-prepared solid-base amino-modified silica aerogel (SA-NH₂) can be used as a high-efficient catalytic system for one-pot sequential reaction of acid-catalyzed benzaldehyde dimethyl acetal hydrolysis and base-catalyzed Henry reaction of nitromethane and intermediate benzaldehyde. The effect of trace water on benzaldehyde dimethyl acetal hydrolysis was evaluated by batch control experiment, and the texture properties of SA-NH₂ were characterized by SEM, TEM, BET and EA. Furthermore, a possible H⁺/-NH₂ coexistence mechanism was given to explain the synergistic effect of H⁺ induced by the interaction between trace water and nitromethane and the solid-base SA-NH₂ in the model reaction. This work provides a new acid/base coexistence model (liquid-acid/solid-base) where the acid part and the base part would not neutralize and inactivate each other, and could give a reference to the follow-up related research.

2. Experimental section

2.1. Materials

(3-Aminopropyl) trimethoxysilane (APTES, 97%) and anhydrous nitromethane (98.5%, GC) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Alcohol, hydrochloric acid, and sodium hydroxide were all of analytical grade and bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). SA was provided by Nano Tech Co,

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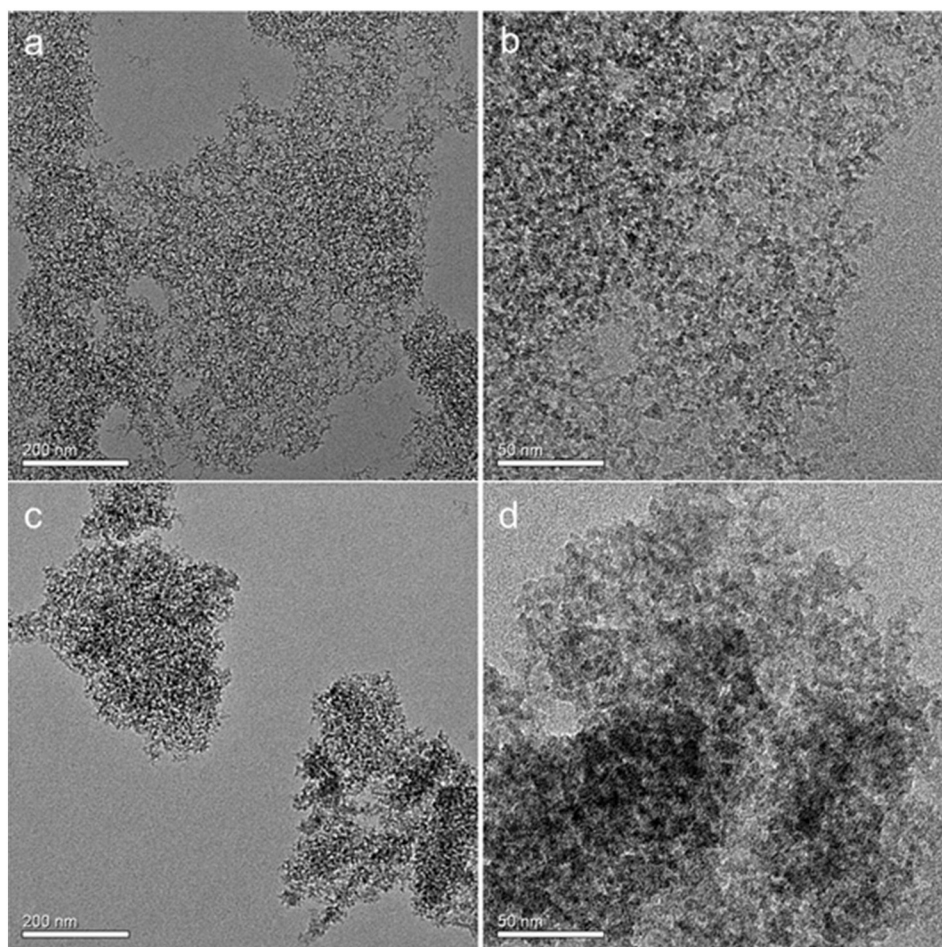


Fig. 1. Transmission electron micrographs of SA (a, b) and SA-NH₂-50 (c, d).

LTD (Shaoxing, China). Benzaldehyde dimethyl acetal (>98.0%, GC), o-xylene (>98.0%, GC), trans-1-nitro-2-phenylethylene (>98.0%, GC), and benzaldehyde (>98.0%, GC) were purchased from TCI (Japan).

2.2. Experimental section

SA was calcined at 823 K for 2 h to remove the organic groups on surface before use. The treated SA powder (100 mg) was dispersed in 100 mL of alcohol by ultrasound for 30 min. Then, x μ L ($x = 25, 50, 100, 150,$ and 300) of APTES was added, and the obtained mixtures were stirred at 30 °C for 24 h. The obtained products were collected by centrifugation, washed with alcohol thrice, and vacuum-dried. The final samples were denoted as SA-NH₂- x , where x represents the added amount of APTES in the synthesis process.

2.3. Characterization

Transmission electron micrographs (TEM) were taken using the JEM-1011 electron microscope operating at an accelerating voltage of 80 kV. Scanning electron micrographs (SEM) and energy dispersive spectra were obtained using the JSM-6360LV scanning electron microscope equipped with an X-act energy-dispersive X-ray (EDX) analyzer (Oxford INCA). N₂ adsorption–desorption isotherms were obtained using a Micromeritics ASAP TriStar II 3020 pore analyzer at 77 K under continuous adsorption conditions. The samples were outgassed at 150 °C for 8 h before measurements. The specific surface areas were calculated by the Brunauer-Emmett-Teller method, and pore size distributions were measured using Barrett-Joyner-Halenda analysis from the

desorption branches of nitrogen isotherms. Elemental analyses of N were performed using a Euro Vector EA3000 elemental analyzer. Infrared (IR) spectra of samples in KBr disks were recorded by a Thermo Nicolet 6700 FT-IR spectrometer. The acid and base contents of the catalyst were determined by acid–base titration method [1,15] as shown in the Supporting Information.

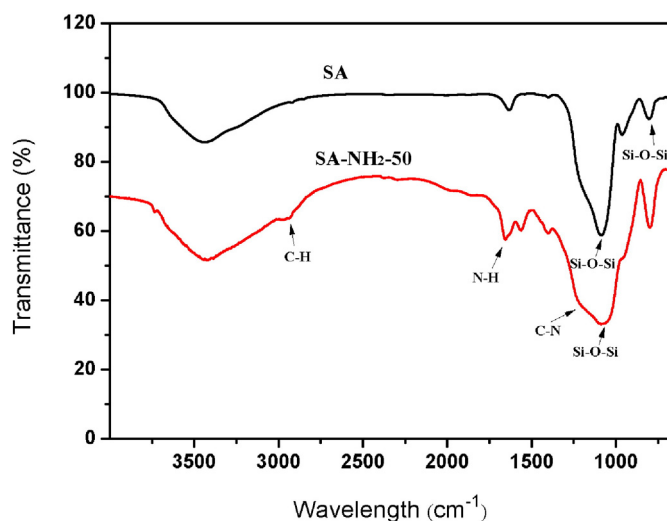


Fig. 2. FT-IR spectra of SA and SA-NH₂-50.

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