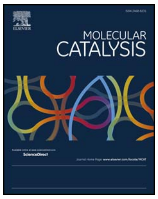
Molecular Catalysis 449 (2018) 31–37

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat



Amine-functionalized MgAl LDH nanosheets as efficient solid base catalysts for Knoevenagel condensation

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ARTICLE INFO

Keywords:
LDH
Nanosheets
Delamination
APTS
Knoevenagel condensation

ABSTRACT

In this work, an efficient base catalyst, amine-functionalized MgAl LDH nanosheet, was prepared by grafting aminopropyltriethoxysilane (APTS) on MgAl LDH nanosheets via the condensation between the ethyoxyl groups of APTS and the hydroxyl groups on the surface of MgAl LDH nanosheets. The physical-chemical properties of the prepared samples were characterized by XRD, FT-IR, N_2 adsorption-desorption, TG, SEM, CO_2 adsorption and catalytic reactions. The results showed that APTS could be successfully grafted on MgAl LDH nanosheets due to their high surface area and more available and accessible $-OH$ groups. The prepared amine-functionalized MgAl LDH nanosheets showed excellent catalytic performance in Knoevenagel condensation due to the synergistic effects among the grafted amine groups, the LDH nanosheets and reaction substrates. Moreover, the prepared catalysts can be used to catalyze various Knoevenagel condensations, and have well reusability. This method supplies an effective way to fabricate novel base catalysts based on LDHs.

1. Introduction

Knoevenagel condensation, one of the most important carbon–carbon bond formation methodologies in synthesis of numerous special chemicals and chemical intermediates [1], is generally catalyzed by homogeneous base catalysts [2–4]. However, the homogeneous catalysts are difficult to be separated and recovered from the reaction mixtures and cannot meet the increasingly stringent requirements for environmental benignity and sustainability. Hence, heterogeneous catalysts, including Lewis acids [5], sulfate-ion promoted zirconia [6], nitrogen doped carbon [7] and amine-functionalized polyacrylonitrile fiber [8], silicas [9,10], MOFs [11], graphene oxide [12], etc, have recently been employed to catalyze Knoevenagel condensation. Among these reported heterogeneous catalysts, various amine-functionalized catalysts have received intense interests. For Knoevenagel condensation, it can proceed on pairs of Lewis basic and acidic sites reaching different activity and selectivity [13]. Therefore, the properties of the supports have significant effects on the catalytic performance of the resultant amine-functionalized materials. The ideal supports not only can provide the anchoring sites for amine groups, but also can bring synergy to facilitate the reaction through the interaction between support and reaction substrates. Gao et al. [14] showed that amine functionalized UiO-66-NH_2 metal–organic frameworks (MOFs) with Lewis acid Zr sites and base $-NH_2$ sites are more active and selective than bare UiO-66 in Knoevenagel condensation of benzaldehyde with malononitrile. ZIF-8 with base sites (derived from 2-methylimidazolate anions) and Lewis acid sites (derived from Zn^{2+} cations) was also found to be beneficial for promoting Knoevenagel condensation [15]. Xia et al. [16] have shown that the incorporation of weak acid sites next to amine-sites is favorable to the overall reaction rate. However, for amine-containing MOFs or ZIF-8, their practical applicability is usually limited to some extent by their intrinsically microporous structures, while for the conventional SiO_2 support, due to its very weak acid sites, normally need introducing new types of hydroxyl groups to engineer the surface silanol groups. Therefore, it is of high importance to develop or select appropriate supports that can optimize the various natures of grafted amine groups, and eventually promote their activity in Knoevenagel reaction.

Layered double hydroxide (LDH), a kind of typical layered clay minerals, is composed of positively charged two-dimensional brucite-type octahedral layers and interlayer anions. LDHs have progressively received much attention as catalysts or supports due to their surface acid–base properties [17–19]. Therefore, LDHs are potential supports for preparation of amine-functionalized catalysts. However, LDHs prepared by the conventional co-precipitation was severely aggregated due to the high surface charge and the hydrophilic of LDH sheets. As a consequence, LDHs usually have low surface areas and cannot provide enough exposed surface hydroxyl groups for grafting amine groups

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https://doi.org/10.1016/j.mcat.2018.02.004
Received 4 September 2017; Received in revised form 8 February 2018; Accepted 8 February 2018
2468-8231/

[20]. To overcome this problem, delamination of LDHs has attracted much attention. After delamination, the obtained LDH nanosheets were highly dispersive and gave large surface areas which not only can increase the anchoring sites for amine groups, but also can facilitate the mass transport of reagents to and from the surface [21,22]. However, LDHs are difficult to be delaminated due to their high formal charge density and the strong interactions between adjacent layers [23–25]. Delamination of LDHs generally needs inserting an anion into the interlayer to increase the interlayer distance by swelling with an appropriate solvent and then delaminating the swollen LDH structure in an appropriate solvent/dispersant medium [24]. Nevertheless, this method suffers from high solvent consumption, low yields and difficult isolation of the delaminated LDH nanosheets from the solvent dispersion while avoiding aggregation. Recently, a new aqueous miscible organic solvent treatment (AMOST) method has been developed for the large-scale high yield synthesis of highly porous dispersed LDH powders containing delaminated nanosheets [26]. This method provides a new opportunity for the application of LDH nanosheets as catalyst supports.

In this paper, amine-functionalized MgAl LDH nanosheets were prepared by grafting APTS onto the surface of LDH nanosheets and used as solid base catalysts for Knoevenagel condensation. The unique acid-basic properties and high surface area of MgAl LDH nanosheets showed significant support advantages as compared to other conventional supports, and the prepared amine-functionalized MgAl LDH nanosheets gave excellent catalytic performance in Knoevenagel condensation.

2. Experimental

2.1. Chemical reagents

Aminopropyltriethoxysilane (APTS), malononitrile, ethyl cyanoacetate, 4-methoxy-benzaldehyde , 1-naphthaldehyde, 4-methyl-benzaldehyde were purchased from Alfa Aesar. SiO_2 and Al_2O_3 were obtained from Nankai University Catalyst Co., Ltd. Other chemical reagents were obtained from Sinopharm Chem. Reagent Co., Ltd. All the reagents were used as received without further purification.

2.2. Catalyst preparation

MgAl LDH nanosheets were synthesized according to the AMOST method described in the literature [26]. 40 mL of aqueous solution of $Mg(NO_3)_2{\cdot}6H_2O$ (30 mmol) and $Al(NO_3)_3{\cdot}9H_2O$ (10 mmol) was dropped into 100 mL of H_3BO_3 solution under vigorous stirring. The pH of the mixture solution was maintained at 9 by adjusting with 1.5 M NaOH solution. The resultant gel-like slurry was stirred at room temperature for 10 min and then aged at 65 °C for 24 h. After filtration, the obtained white solid product firstly was washed with deioned decarbonated water (DD water) until neutral, and then was washed with acetone and dried at 65 °C overnight. The obtained sample was denoted as MgAl-LDH-NS. For comparison, the conventional MgAl-LDH sample was also prepared by the coprecipitation method [27], and the obtained sample was denoted as MgAl-LDH.

APTS functionalized sample was prepared according to the literature with some modification [28]. Typically, 30 mL of toluene was added to 1.0 g of support (MgAl-LDH-NS, MgAl-LDH, Al_2O_3 or SiO_2) at 110 °C in an oil bath under Ar flow. After stirring for 0.5 h, 2.168 mmol of APTS dissolved in 20 mL of toluene was added and the mixture was continuously stirred for 12 h. After that the sample was extracted by ethanol for 24 h and dried at 80 °C overnight. The obtained sample was denoted as NH_2-MgAl-LDH-NS, NH_2-MgAl-LDH, NH_2-Al_2O_3 and NH_2-SiO_2, respectively. By adjusting the APTS amount (APTS/LDH = 0.542, 1.084 and 4.336 mmol/g) in the grafting process, a series of NH_2-MgAl-LDH-NS samples with different $-NH_2$ amounts were prepared. The obtained samples were denoted as NH_2-MgAl-LDH-NS-1, NH_2-MgAl-LDH-NS-2 and NH_2-MgAl-LDH-NS-3, respectively.

2.3. Characterization

Powder X-ray diffraction (XRD) measurement was performed on a Shimadzu XRD-6000 diffractometer by using Cu Kα radiation over a 2θ range from 5 to 65 °. FT-IR spectra were recorded by a SHIMADZU FTIR-Affinity-1 spectrometer using the conventional KBr pellet method. Scanning electron microscopy (SEM) image was taken on a Hitachi S-4800 instrument. N_2 adsorption was performed at 77 K using a Quantachrone Nova 1200e apparatus and the surface area was calculated by the BET method. CO_2 adsorption was carried out at 25 °C on a Quantachrone Nova 1000 apparatus. The sample was evacuated at 150 °C for 5 h before N_2 or CO_2 adsorption measurement. TG analysis was carried on a STA 449 F3 between 25 and 650 °C with a heating rate of 10 °C/min under air atmosphere. The N contents of NH_2-Al_2O_3 and NH_2-SiO_2 were determined by a varioELcube elemental analyzer and N contents of NH_2-MgAl-LDH and NH_2-MgAl-LDH-NS were calculated from the Si contents measured by inductively coupled plasma (ICP) analysis.

2.4. Catalytic reaction

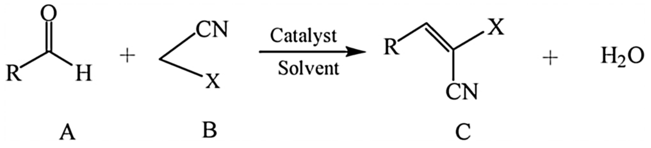
Knoevenagel condensation between benzaldehyde/4-methoxy-benzaldehyde/4-methyl-benzaldehyde/1-naphthaldehyde and malononitrile (X = CN)/ethyl cyanoacetate (X = COOEt) (Scheme 1) was carried out in a 25 mL two-neck flask with a magnetic stirring bar and condenser. Typically, the powdered catalyst (0.06 g) was added to 10 mL of toluene containing two kinds of substrates (1.9 mmol, respectively), and then the mixture was stirred in a thermostatic water bath. After reaction, the catalyst was separated by centrifugation, and the liquid products were identified by a GCMS-QP2010 SE and analyzed using a SHIMADZU GC-2014 equipped with a FID detector and a RTX-1 capillary column. The separated products from the reaction with ethyl cyanoacetate as the substrate were analyzed by ^{1}H NMR. ^{1}H NMR spectra were recorded on Bruker Avance III (400 MHz) instrument with $CDCl_3$ as the solvent.

3. Results and discussion

3.1. Characterization

3.1.1. XRD

The XRD patterns of the prepared different samples are shown in Fig. 1. As shown in Fig. 1, MgAl-LDH prepared by the conventional coprecipitation method showed the typical LDH diffraction peaks. No characteristic Bragg reflections of LDHs was observed in the XRD pattern of MgAl-LDH-NS obtained by AMOST method, whereas a series of LDH characteristic diffraction peaks appeared upon treating MgAl-LDH-NS with Na_2CO_3 aqueous solution, even if these diffraction peaks significantly widen. These results indicated that MgAl-LDH-NS was completely delaminated into single sheets [26], and the delaminated LDH nanosheets could restacked into their layered structure in Na_2CO_3 aqueous solution. Upon grafting APTS, the obtained NH_2-MgAl-LDH and NH_2-MgAl-LDH-NS displayed almost the same reflections as their precursors. However, different from MgAl-LDH-NS, only very weak LDH characteristic reflections were observed upon treating NH_2-MgAl-LDH in Na_2CO_3 aqueous solutions, indicating that APTS grafted on MgAl-LDH-NS seriously influenced the restack of LDH nanosheets and decreased the order degree of the restacked sample. This perhaps



Scheme 1. Knoevenagel condensation.