ZnAl$_2$O$_4$@SiO$_2$ nanocomposite catalyst for the acetylation of alcohols, phenols and amines with acetic anhydride under solvent-free conditions

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A ZnAl$_2$O$_4$@SiO$_2$ nanocomposite was prepared from metal nitrates and tetraethyl orthosilicate by the sol-gel process, and characterized by X-ray diffraction, Fourier transform infrared, transmission electron microscopy, and N$_2$ adsorption-desorption measurements. The nanocomposite was tested as a heterogeneous catalyst for the acetylation of alcohols, phenols, and amines under solvent-free conditions. Under optimized conditions, efficient acetylation of these substrates with acetic anhydride over the ZnAl$_2$O$_4$@SiO$_2$ nanocomposite was obtained. Acetylation of anilines and primary aliphatic amines proceeded rapidly at room temperature, while the reaction time was longer for the acetylation of alcohols and phenols, showing that an amine NH$_2$ group can be selectively acetylated in the presence of alcoholic or phenolic OH groups. The catalyst can be reused without obvious loss of catalytic activity. The catalytic activity of the ZnAl$_2$O$_4$@SiO$_2$ nanocomposite was higher than that of pure ZnAl$_2$O$_4$. The method gives high yields, and is clean, cost effective, compatible with substrates having other functional groups and it is suitable for practical organic synthesis.

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1. Introduction

The selective protection of alcohols, phenols, and amines has received attention for its fundamental importance and also for its role in multistep synthesis [1,2]. This important transformation is typically performed using acetic anhydride and/or acetyl chloride in the presence of either basic or acidic catalysts. Numerous catalytic systems are available for this transformation [3–13], but most of these are homogeneous catalysts and non-recoverable, and they have the disadvantages of prolonged reaction time, low yields, harsh conditions, use of harmful organic solvents, tedious work-up procedures, excessive reagents or catalysts, and the use of explosive, moisture-sensitive, or expensive catalysts.

One of the most promising solutions to overcome these problems is the use of heterogeneous solid catalysts [14,15], which can be recovered easily from the reaction mixture by simple filtration and reused to make the process more economical and environmentally viable. Solid catalysts such as H$_2$O$_x$–SiO$_2$ [16], montmorillonites [17–19], metal oxides [20–22], H$_2$SO$_x$–SiO$_2$ [23], zeolites [24,25], HBF$_4$–SiO$_2$ [26], MoO$_2$–Al$_2$O$_3$ [27], NaHSO$_x$–SiO$_2$ [28], sulphated zirconia [29], (NH$_4$)$_2$SiH$_2$PO$_x$[30], silica-bonded Co(II) salen [31], silica-bonded N- and S-propyl sulfamic acids [32,33], poly(4-vinylpyridinium) perchlorate [34], polystyrene-supported GaCl$_3$ [35], borated zirconia modified with ammonium metatungstate [36], rice husk [37], V(IV) tetraphenylporphyrin [38], Ti(IV)salophen)(OTf)$_2$ [39], polystyrene-bound electron-defi-
cient Sn(IV) porphyrin [40], poly(vinylpolypyrrolidinium) tribromide [41], modified attapulgite [42], succinimide-N-sulfonic acid [43], acylimidazolium acetate [44], Ph₃P(O)Ac₂ [45], poly(4-vinylpyridinium) tribromide [46], sulfonated nanoparticles [48] and Ni/Silica [49], Cu based metal-organic framework [50] have been used in the acetylation of alcohols, phenols, and amines. However, each of these catalysts or reagents has disadvantages and limitations.

In recent years, transition metal mixed oxides with the perovskite (ABO₃) or spinel (AB₂O₄) structure have attracted considerable attention as promising catalystic materials for organic transformations due to their high thermal and hydrothermal stability and relatively low cost compared with their noble metal counterparts [51–56]. However, their potential catalytic stability and relatively low cost compared with their noble metals cannot be ignored.

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2. Experimental

2.1. Preparation of the catalyst

The reagents used in the synthesis of ZnAl₂O₄@SiO₂ were Al(NO₃)₃·9H₂O, Zn(NO₃)₂·6H₂O, and tetraethylorthosilicate (Si(OC₂H₅)₄, TEOS, >99.5%). All these reagents were of purity >98% from Merck. Alcohols, phenols, amines, and solvents were purchased with the highest purity available (>98%) from Merck Chemical Company and used without further purification.

The ZnAl₂O₄@SiO₂ nanocomposite was synthesized by the sol-gel method as follows. A mixture of TEOS (0.35 mol, SiO₂ content 21 g), ethanol (60 mL), and water (10 mL) was prepared in a 1-L beaker, and its acidity was adjusted to pH 2 using nitric acid (0.1 mol/L). In order to hydrolyze the TEOS, the mixture was stirred at room temperature for 1 h. Then, a solution of Al(NO₃)₃·9H₂O (0.05 mol, 18.75 g) and Zn(NO₃)₂·6H₂O (0.025 mol, 7.27 g) dissolved in 90 mL of water was added. The resulting mixture was stirred for 1 h and allowed to gel at room temperature over 5 d. After gelation, it was dried and calcined at 600, 800, or 900 °C for 5 h. It is clear that the sample calcined at 600 °C was amorphous, with one broad reflection at 2θ = 22.5°, which is the characteristic diffraction of the amorphous SiO₂ matrix. Calcining the dried gel sample at 800 °C resulted in gradual crystallization of the sample. The increase of calcination temperature to 900 °C resulted in an increase in the crystallinity. All the peaks could be indexed as the (220), (311), (400), (422), (511), and (440) planes assigned to the ZnAl₂O₄ spinel (ICCD Card File No. 5-0669). No other crystalline phase was detected in the calcined samples. The result meant that the materials consisted of ZnAl₂O₄ nanocrystals and an amorphous phase of SiO₂. Furthermore, the diffraction peaks of the ZnAl₂O₄ phase were markedly broadened due to the small size of the particles. The average particle size calculated based on the Debye-Scherrer equation [60] using the radial distribution function of the XRD patterns.

2.2. Characterization of the catalyst

X-ray diffraction (XRD) patterns were recorded on a Rigaku D‐max C III X‐ray diffractometer using Ni‐filtered Cu Kα radiation (λ = 1.5406 Å) to determine the phases in the samples. Infrared (IR) spectra were recorded on a Shimadzu system FT–IR 160 spectrophotometer using KBr pellets. The particle size and morphology of the ZnAl₂O₄@SiO₂ nanocomposite were determined by a transmission electron microscope (TEM, Philips CM10) with an accelerating voltage of 80 kV. To prepare the TEM specimen, a small amount of the powder was dispersed in ethanol in an ultrasonic bath for 30 min, and a few drops of the resulting suspension were placed on a carbon coated copper grid. The specific surface area of the catalyst was obtained by the BET method using N₂ adsorption-desorption at -196 °C with a surface area analyzer (Micromeritics ASAP 2010). Before each measurement, the sample was degassed at 200 °C for 1 h.

3. Results and discussion

3.1. Characterization of the ZnAl₂O₄@SiO₂ nanocomposite

Figure 1 shows the XRD patterns of the ZnAl₂O₄@SiO₂ samples calcined at 600, 800, and 900 °C for 5 h. It is clear that the sample calcined at 600 °C was amorphous, with one broad reflection at 2θ = 22.5°, which is the characteristic diffraction of the amorphous SiO₂ matrix. Calcining the dried gel sample at 800 °C resulted in gradual crystallization of the sample. The increase of calcination temperature to 900 °C resulted in an increase in the crystallinity. All the peaks could be indexed as the (220), (311), (400), (422), (511), and (440) planes assigned to the ZnAl₂O₄ spinel (ICCD Card File No. 5-0669). No other crystalline phase was detected in the calcined samples. The result meant that the materials consisted of ZnAl₂O₄ nanocrystals and an amorphous phase of SiO₂. Furthermore, the diffraction peaks of the ZnAl₂O₄ phase were markedly broadened due to the small size of the particles. The average particle size calculated based on the Debye-Scherrer equation [60] using the radial distribution function of the XRD patterns.