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Amino functionalized chitosan as a catalyst for selective solvent-free self-condensation of linear aldehydes

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ABSTRACT

An aminopropyltrimethoxysilane functionalized chitosan was found to be an efficient solid base catalyst for the self-aldol condensation of linear aldehydes under solvent-free conditions. The modified catalyst was characterized using physical techniques, elemental analysis, FT-IR, and TGA. The modified chitosan was evaluated for the aldol condensation of C_3–C_7 linear aldehydes in which the selective formation was obtained for α,β-unsaturated aldehydes. A decreasing trend in the conversion from propanal to heptanal was observed. Propanal and pentanal were subjected for detail investigations to study the effect of parameters like amount of catalyst and aldehyde, and temperature on the conversion and selectivity. Kinetic performance of the modified chitosan investigated for a representative aldehyde, pentanal showed that the rate was increased with the catalyst amount, pentanal and temperature. The catalyst was reused up to six cycles without significant loss in its activity and selectivity.

1. Introduction

Aldol condensation is an important reaction in organic synthetic chemistry due to the formation of carbon–carbon bonds during the reaction process. This type of reaction may occur via self-condensation between two of the same aldehyde or ketone molecules or via cross-condensation between two molecules of different aldehydes or ketones [1–3]. Such a reaction usually proceeds over basic or acidic catalysts such as sodium hydroxide or sulfuric acid in the liquid phase. However, the disadvantages of such a process include corrosion, safety hazards, separation procedures, and environmental problems due to the use of sodium hydroxide or sulfuric acid. Therefore, the use of solid bases or acids has drawn increasing interest during the past three decades [4–9]. The solid base catalysts generally used for aldol condensations include MgO [10], hydrotalcites [11,12] and synthetic talc [13].

Self-condensations of aldehydes are important in the view of industrial applications. These products find applications in the fields of pharmaceuticals, fragrances, plasticizers, detergents and cosmetics. The synthesis of 2-ethylhexenal and its hydrogenated product 2-ethylhexanol from self-condensation of butanal find its use in soap, detergent, plasticizers, coatings, adhesives, dioctyl-phthalate and specialty chemical industries [14]. Another important aldol product is aldol intermediate of pentanal which is commercially important product and finds use in the synthesis of plasticizer and detergent alcohols [15].

The aim of present investigation is to develop a suitable solid base catalyst for aldol condensation of linear aldehydes in solvent-free environment. Chitosan is a polyaminosaccharide, normally obtained by alkaline deacetylation of chitin [16]. Chitosan, even having a large amount of $-NH_2$ group, is not found to be effective for base catalyzed reactions [17]. The generally used method is to treat with HCl and then to form chitosan beads by adding it into the NaOH solution. It will be a better choice to functionalize the chitosan avoiding the use of acids and alkalis to obtain active base catalyst. Therefore, modified chitosan was synthesized by modification with aminopropyltrimethoxysilane (APTMS), characterized and investigated as solid base catalyst for self-aldol condensation of C_3–C_7 linear aldehydes.

2. Experimental

2.1. Materials

The aldehydes propanal (98%) from Loba chemie, India, butanal (99%) from s.d. Fine Chemicals, India, and pentanal (97%), hexanal (98%), heptanal (95%) from Sigma–Aldrich, USA, were obtained. Toluene (99.5%) was obtained from Fisher Scientific, India. Aminopropyltrimethoxysilane (97%) and chitosan were purchased from Sigma–Aldrich, USA. All the chemicals were used as such.

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2.2. Catalyst synthesis

Amino functionalization of the chitosan was done by treating chitosan with APTMS. In a typical procedure 1.5 g chitosan and 1 g APTMS was taken in 25 ml toluene in a 50 ml round bottom flask (RBF). The RBF was connected with a water condenser and an inert atmosphere was created by nitrogen. The RBF under an inert atmosphere was refluxed in an oil bath at 110 °C. The refluxing was continued for 24 h with stirring at 450 rpm. After 24 h, the flask was cooled to room temperature. The catalyst was filtered, dried at 100 °C and powdered to get the amino functionalized chitosan (CHM).

2.3. Characterization of the catalysts

Fourier transform infrared spectra (FT-IR) were recorded with Perkin-Elmer, GX-FTIR using KBr pellet. Elemental (C, H, N) analysis of chitosan and modified chitosan was carried out with Perkin-Elmer CHNS/O analyzer (Series II, 2400). Thermogravimetric analysis (TGA) was done using Mettler Toledo TGA/SDTA 851e equipment in flowing nitrogen (flow rate, 50 mL/min), at a heating rate of 10 °C/min. N_2 sorption analysis was carried out at 77.4 K in a sorptometer (ASAP 2010, Micromeritics). The sample was degassed at 120 °C for 4 h prior to the sorption analysis.

2.4. Aldol condensation

Weighed amount of aldehyde and catalyst was taken in an oven dried 50 ml double necked round bottom flask. One neck of the flask was fitted with refluxing condenser having spiral tube inside and another neck of the flask was blocked with silicon rubber septum. The top of the refluxing condenser was connected to balloon filled with nitrogen. The entire experimental setup was kept in an oil bath equipped with temperature and agitation speed controlling units. The water at 15 °C was circulated in refluxing condenser throughout the course of reaction from a water chiller at the flow rate of 6 L/min. The reaction was carried out at 100 °C for 8 h. The silicon grease was used in all joints to prevent the vapor loss of reaction mixture and progress of the reaction was monitored in terms of consumption of aldehyde. The analysis of product mixture was carried out by gas chromatography (GC) (Shimadzu 17A, Japan) and GC–MS (mass spectrometer, Shimadzu-QP2010, Japan). The GC has a 5% diphenyl and 95% dimethyl siloxane universal capillary column (60 m length and 0.25 mm diameter) and a flame ionization detector (FID). The initial column temperature was increased from 40 to 200 °C at the rate of 10 °C/min. Nitrogen gas at a flow rate of 100 mL/min was used as the carrier gas. The temperatures of the injection port and FID were kept constant at 200 °C during the product analysis. The retention times of different compounds were determined by injecting pure compounds under identical GC conditions.

2.5. Kinetics

Kinetic experiments were carried out in an oven dried double necked round bottom flask in which desired amounts of aldehyde and catalyst were taken. The flask was kept in an oil bath having provision for control of temperature and agitation speed. During the course of the reaction aliquots were taken out at different time intervals and the analysis of product mixture was carried out by GC. The kinetics was investigated in detail as a function of temperature and the catalyst amount and aldehyde. To ensure the reproducibility of condensation reaction, repeated experiments were carried out under identical reaction conditions. The results obtained, including conversion and selectivity data were found to be reproducible within 5% variation.

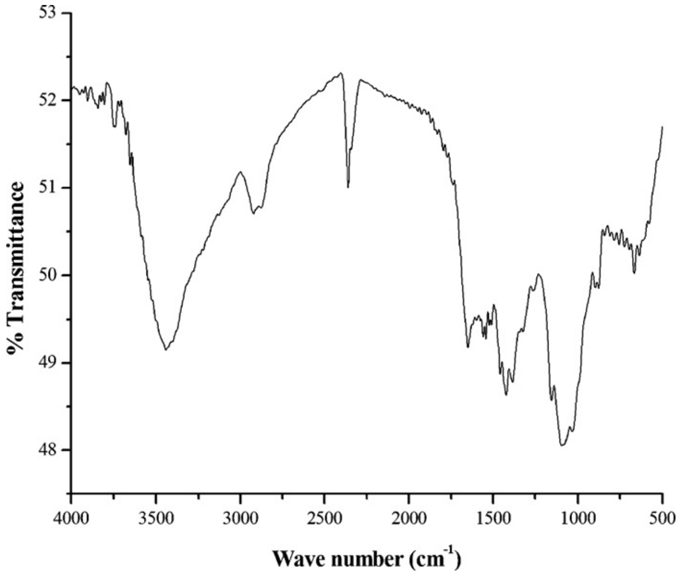

Fig. 1. FT-IR spectrum of CHM.

3. Result and discussion

3.1. Characterization of the catalysts

3.1.1. FT-IR analysis

The FT-IR spectrum of CHM (Fig. 1) showed distinctive absorption band at 1542 cm^{-1} for $-NH_2$ bending. The absorption bands at 1154 cm^{-1} (anti-symmetric stretching of the C–O–C Bridge), 1093 and 1026 cm^{-1} (skeletal vibration involving the C–O stretching) are characteristics of its saccharide structure [18]. The absorption bands at 3441, 2921 cm^{-1} are attributed to O–H and methylene ($-CH_2$) group respectively.

3.1.2. Thermogravimetric analysis

The thermal behavior of CHM is shown in Fig. 2. Chitosan has two main weight losses with one starting at 80 °C and another starting at around 260 °C. The first weight loss of 5% is attributed to the

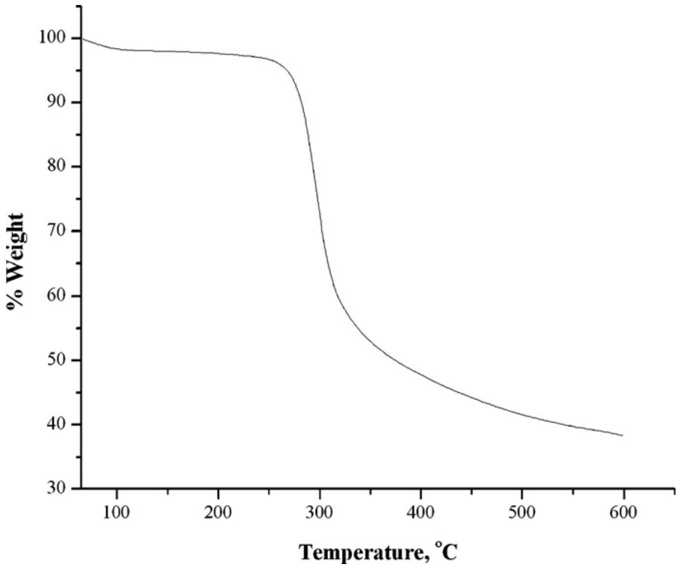

Fig. 2. TGA of CHM.