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Chitosan as a biodegradable heterogeneous catalyst for Knoevenagel condensation for benzaldehydes and ethylcyanoacetamide

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Abstract

A natural biopolymer chitosan is being employed *is* betwerogeneous solid base catalyst for the Knoevenagel condensation reaction between benzoldehyde and cyanoacetamide under mild reaction conditions. This reaction offers the duct synthesis of condensation product with two functional groups that can readily be *Pact* onalized. The biopolymer is used for five cycles with no decrease in activity and tot altration test proves heterogeneity of the reaction. Some of the salient features of this subtrate groups include biodegradability of catalyst, high catalyst stability, mild reaction conditions and wide substrate scope. The structural integrity is retained even after repeated cycles as evidenced by powder X-ray diffraction (XRD).

Keywords: Biopolymer; Chitosan; Heterogeneous Catalysis; Knoevenagel condensation; Solid base

1. Introduction

Among the wide ranges of naturally occurring biopolymers, chitosan is one of the biopolymers that have attracted researchers for many applications due to their attractive properties like non-toxicity, biocompatibility and biodegradability. Further, chitosan exist in a three dimensional structure with functional groups such as amino and hydroxyl groups in its skeleton. These functional groups in chitosan are often used as anchoring sites for further functionalization or active sites in promoting organic reactions. Among the various applications of chitosan, the use of chitosan as heterogeneous callyst is highly promising due to its insoluble nature in water and common organic solventy. Hence, chitosan or modified chitosan has been employed as heterogeneous cata ysts for various organic transformations. For example, Cu-metal-organic framework supported on chitosan was used for condensation reaction,[1] Knoevenagel condensation reactions were performed with chitosan, [2-4] modified chitosan-based hydrogels weir also employed to perform Knoevenagel condensation, [5] chitosan hydrogel was used for aldol reactions, [6] chitosan-TiO₂ hybrid catalyst was reported for nitroak of condensation, [7] chitosan was employed as solid catalyst for the synthesis of jasminak'-hyde,[8] chitosan biohydrogel beads were reported for C-C bond reaction, [9] carbo xyn thyl chitosan Schiff-base palladium(II) catalyst was used for Suzuki-Miyaura cross-co pling,[10] melamine-functionalized chitosan was used to obtain cyanocinnamonitrile, [11] multicomponent synthesis realized with chitosan as solid catalyst under microwave conditions for the synthesis of bis(2-amino-tetrahydro-4H-chromene-3carbonitrile,[12] chitosan-based Schiff-base Ni complex was shown to promote the synthesis of pyrazolophthalazinediones [13] and chitosan-supported Cu(II) Schiff-base for the synthesis of 5-substituted 1H-tetrazoles and homocoupling of terminal alkynes.[14]

Knoevenagel condensation is one of the well-known C-C bond forming reactions in organic chemistry which is performed between carbonyl compounds and active methylene

compounds and the resulting condensation product finds application in polymers and pharmaceuticals. Furthermore, the most frequently used active methylene compounds for Knoevenagel condensation reaction were malononitrile and ethylcyanoacetate catalyzed by acids or bases either in homogeneous or in heterogeneous fashion. Hence, this reaction is considered as one of the benchmark reactions to rank different catalysts. This reaction has been reported with a wide range of heterogeneous solid catalysts like mesoporous silica, [15] microporous titanosilicate,[16] methylammonium-FAU zeolite,[17] rare-earth exchanged nitrided NaY zeolite,[18] Cs-NaY,[19] ITQ-2,[201 1. resoporous sodalite,[21] aluminophosphates oxynitrides, [22] alkali metal-modif ea oxide, [23] mesoporous K-ZrO₂,[24] amine modified graphene oxide,[25] hexagonal boron nitride,[26] nickel iron hydrotalcite, [27] IRMOF-3, [28] MIL-53(Al)-NH₂ [25] and MIL-100(Fe). [30] Although considerable numbers of reports have been r.p. tred for Knoevenagel condensation reaction, some of the main limitations are tediour synthesis procedure of catalyst, easy deactivation, high expensive nature, requires activation of catalyst prior catalytic test and limited substrate scope. Considering these limitations in the reported methods, there is still a scope for the development of a simple and facile heterogeneous catalyst from naturally occurring biopolymer to promote this reaction.

In the present wo k, chitosan is employed as an eco-friendly heterogeneous solid base catalyst for the Knoevenagel condensation reaction between benzaldehyde and cyanoacetamide under mild reaction conditions. Although this reaction has been effectively promoted between benzaldehyde and malononitrile, no reports are available in the literature for the condensation between benzaldehyde and cyanoacetamide. This reaction is an important reaction since the resulting product has two different functional groups for further synthetic modifications. Besides, this condensation reaction has many benefits including the

employment of a naturally available biopolymer as heterogeneous catalyst, environmentally benign, absence of functionalization and it is commercially available.

2. Experimental Section

2.1 Material

Chitosan, cyanoacetamide and aldehydes were purchased from Sigma Aldrich, Alfa Aesar and Merck, used as received without any purification. Ethanol, water and other solvents were procured from Chemical Drug House and Sisco Research Laboratory and used without any additional purification.

2.2 Instruments

The powder XRD patterns were measured in the refraction mode in a Bruker D2 Phase X-ray diffractometer (30 kV, 10 mA) using the Cu K α ($\lambda = 1.5406$ Å) radiation. FT-IR analysis was carried out with Bruker tensor 27 series FT-IR spectrometer in the region of 400-4000 cm⁻¹ with 2 cm⁻¹ resolution ark¹ 16 scans. SEM images were collected using a Hitachi S-3000H scanning electron arcocope. Conversion and selectivity were determined by Agilent 7820A gas chromatography (GC) using HP-5 column of 30 m length and high pure nitrogen as carrier gas with flame ionization detector. Finally, the obtained products were confirmed by 589(A hodel of Agilent GC-MS instrument using HP-5 column of 30 m length and high pure heliur gas as carrier gas. ¹H and ¹³C NMR Avance III HD Nanobay 400 MHz FT-NMR spectrometer using DMSO-d₆ and CDCl₃ appropriately based on the solubility of the compounds.

2.3 Catalytic procedure Knoevenagel condensation between 1 and 2

A 10 mL schlenk tube was charged with chitosan (20 mg), **1** (0.5 mmol) and **2** (0.6 mmol). To this mixture 1:1 ratio of water and ethanol (0.4 mL) was added and these mixtures were homogeneously mixed. This slurry was then placed in an oil bath maintained at 70 $^{\circ}$ C for 4 h. The kinetics of the catalytic reaction was monitored by collecting samples at different

time intervals from the reaction mixture and analyzed by GC using 7820A model instrument. Also, the yields of the resulting products were determined by GC using internal standard method. Finally, the observed products were identified using Agilent 5779B GC-MS technique. The catalyst was reused in subsequent cycles after recovering the solid from the reaction mixture, washed three times with absolute ethanol (5 mL x 3) followed by drying at 80 °C for 2 h. Later, this dried solid catalyst was subjected for reusability tests with the fresh reactants **1** and **2** in the next cycle. The as-synthesized products were characterized by ¹H-NMR, ¹³C-NMR and GC-MS techniques and copies of these cpectra are provided in Figures S1-S33.

3. Results and discussion

To verify the structural features of chitogan, series of characterization methods like elemental analysis, powder X-ray diffiction (XRD), Fourier Transform infrared spectroscopy (FT-IR) and scanning election microscope (SEM) were conducted and the observed results are discussed belov. Exmental composition of chitosan was measured and the atomic weight percentages of C, H and N remained identical with earlier data as well as matched with the data provided by commercial supplier. The structural integrity and the physical nature of chito an were ascertained by performing powder XRD analysis and the observed results are shown in Figure 1. As it can be seen in Figure 1, two broad diffraction patterns are seen at around 10 and 20 degrees, suggesting amorphous nature of chitosan. But, the positions of 2θ values of these two broad peaks have slightly altered after the reaction, but it is retained during the reusability tests. In any way, these changes in the structural skeleton did not affect its catalytic performance. Further, chitosan was also characterized by FT-IR to understand the existence of various functional groups and the observed results are shown in Figure 2. The characteristic stretching frequencies like O-H, N-H and C-H stretching frequencies were observed at around 3300-3500, 3200-3300 and 2900 cm⁻¹, respectively. In

addition to these bands, C-H bending vibration is also seen at 1450 cm⁻¹. These characteristic stretching frequencies indicate the presence of O-H in the form of primary alcohols, free amino groups and C-H in glucose units. Thus, the recovered chitosan after the catalytic reaction and reused chitosan did not show many changes in its skeleton thus indicating the absence of organic products on chitosan.



Figure 1. Powder XRD patterns of (a) fresh, (b) recovered after the reaction and (c) five times used chitosan. **Reaction conditions**: 1 (0.5 mmol), 2 (0.6 mmol), chitosan (20 mg), ethanol:water (0.4 mL), 75°C, 4 h.



Figure 2. FT-IR spectra of (a) fresh, (b) recovered and the reaction and (c) five times used chitosan. **Reaction conditions**: 1 (0.5 mmol) (0.6 mmol), chitosan (20 mg), ethanol:water (0.4 mL), 70 °C, 4 h.

Benzaldehyde (1) and cyapercechmide (2) were selected as model substrates to evaluate the catalytic performance of chitosan in the Knoevenagel condensation reaction. This reaction was optimized with respect to various solvents, effect of temperature and catalyst loading. A blank experiment in the absence of chitosan exhibited around 20 % of the expected condensation product at 70 °C after 4 h. Later, the catalytic performance of chitosan was tested for the reaction between 1 and 2 in methanol and ethanol was 54 and 79% yield, respectively under identical conditions. The product yield was enhanced to 86% in water under similar conditions. Then, the reaction between 1 and 2 using chitosan as catalyst in water/ethanol (1:1) mixture afforded 97% yield under identical conditions while the corresponding blank control in the absence of chitosan provided 26% yield. These catalytic results certainly indicate that this condensation reaction is catalyzed by the basic sites present in chitosan. The expected condensation product reached to 65% yield in the presence of

chitosan for this reaction in toluene. Further, the reaction of **1** and **2** showed comparatively lower yields in acetonitrile, THF, 1,2-dichloroethane of 33, 7 and 4%, respectively. Finally, the activity of chitosan in the condensation of **1** and **2** in DMF and DMSO was 52 and 61% yields, respectively under similar conditions. Hence, the optimum conditions to achieve high activity with chitosan were the use of water/ethanol mixture at 70 °C in 4 h. These conditions were further used to optimize catalyst loading and effect of temperature.

Table 1. Optimization of the reaction conditions for Knoevenagel condensation between 1 and 2 using chitosan as solid heterogeneous base catalyst.^a



^aReaction conditions: 1 (0.5 mmol), 2 (0.6 mmol), chitosan (20 mg), solvent (0.4 mL), 70 °C, 4 h; ^bYield was determined by GC using internal standard method; ^c1 : 1 solvent ratio was used; ^dBlank control experiment.

One of the important parameters to be optimized in identifying suitable reaction conditions in heterogeneous catalysis is catalyst loading. In this aspect, four different loadings of chitosan were tested for the condensation between **1** and **2** at 70 °C in water/ethanol mixture. Figure 3 shows the time yield profile for all these catalyst loading under similar conditions. These catalytic results confirm that the evolution of product yield gradually increases upon increasing the catalyst loading and the maximum yield was

observed with 20 mg of chitosan. These data suggest that the number of active sites is higher with 20 mg catalyst loading compared to other loadings under identical conditions, thus showing the highest catalytic activity. Later, the performance of chitosan in promoting the Knoevenagel condensation between **1** and **2** was also optimized at three different temperatures like room temperature, 50 and 70 °C. The observed catalytic profile is shown in Figure 4. The condensation product yield gradually enhanced to achieve quantitative yield upon increasing the reaction temperature from room temperature to 70 °C in water/ethanol mixture with 20 mg catalyst loading.



Figure 3. Effect of catalyst loading for the Knoevenagel condensation between 1 and 2 (a) 5 mg (b) 10 mg (c) 15 mg and (d) 20 mg. **Reaction conditions**: 1 (0.5 mmol), 2 (0.6 mmol), ethanol:water (0.4 mL), 70 °C, 4 h.



Figure 4. Effect of temperature for the Knoevenage' concensation between 1 and 2 (a) room temperature (b) 50 °C and (c) 70 °C. **Rea**tion conditions: 1 (0.5 mmol), 2 (0.6 mmol), chitosan (20 mg), ethanol:water (0.4 mL), ^{*} h.

Hot filtration test (leaching det, is one of the mandatory tests to be performed in heterogeneous catalysis mainly to ascertain that the catalytic reaction is driven by the active sites located in the solid cata st and not due to the leached active sites in the reaction mixture. Hence, this tes was also performed under the optimized reaction conditions. The condensation reaction was initiated between **1** and **2** in water/ethanol mixture using chitosan as catalyst at 70 °C and chitosan was removed at reaction temperature from the reaction mixture after 30 min. Then, the reaction mixture without chitosan was continued up to 4 h and aliquots were periodically withdrawn from the reaction mixture. These aliquots were analyzed by GC. Comparison of the activity with and without catalyst proved that the evolution of the condensation yield is totally inhibited upon removal of chitosan from the reaction the reaction medium (Figure 5). These catalytic data indicate that no active sites are leached to the solution and hence, no activity is observed after removal of the catalyst. Hence, it can be

claimed that the reaction is promoted by the active sites located on chitosan and the catalytic reaction is heterogeneous in nature under these conditions.

Reusability tests are performed very often in heterogeneous catalysis to prove catalyst stability. In this aspect, chitosan stability in this reaction was checked by performing reusability test under the optimized reaction conditions. The catalytic reaction was started under optimized conditions and the catalyst was recovered by filtration, washed and dried. This recovered solid was reused in the subsequent cycle with fresh **1** and **2**. In this way, chitosan was used up to five cycles with no apparent dectry in its catalytic activity (Figure S34). These results indirectly indicate that the structural one of the reaction as well as in the reusability tests. This hypothesis was further verified by characterizing the reused complets by powder XRD, FT-IR, SEM and comparing with the fresh chitosan. Although non-changes have been observed in the XRD patterns of the used sample than the fresh solid, SEM image of the used chitosan exhibits a similar morphology to the fresh solid was. Furthermore, the atomic weight percentages of the elements (C, H and N) remain phoset similar with that of the fresh solid by EDX analysis.



Figure 5. Time yield plots for the Knoevenage¹ condensation between 1 and 2 (a) in the presence of chitosan as a solid base cataly.⁺ (b) hot filtration test and (c) blank control experiment in the absence of chitosan. **K**. **action conditions**: 1 (0.5 mmol), 2 (0.6 mmol), chitosan (20 mg), ethanol:water (0.4 ...⁺), 70 °C, 4 h.



Figure 6. SEM images of (a) fresh and (b) five times used chitosan. **Reaction conditions**: **1** (0.5 mmol), **2** (0.6 mmol), chitosan (20 mg), ethanol:water (0.4 mL), 70 °C, 4 h.

These interesting results encouraged us to expand the scope of chitosan with other substrates bearing electron withdrawing and donating substituents under optimized reaction conditions. The observed catalytic data are given in Table 2. The reaction of 1 and 2 afforded 97% yield in the presence of chitosan as heterogeneous solid catalyst in water/ethanol mixture at 70 °C after 4 h. Under similar conditions, 4-methyl, 4-methoxy and 4-tbutylbenzaldehydes reacted with 2 efficiently to provide respective condensation products in 95, 96 and 89% yields, respectively. The reaction of 2-hydroxybenzaldehyde and 2 afforded the corresponding 53% yield of the condensation product. This moderate activity of this substrate is believed to be due to the intramolecular hydrogen bonding between carbonyl and hydroxyl groups, thus lowering the reactivity of carbonyl group with 2. On other hand, 4nitro and 4-bromobenzaldehydes provided their repettive condensation products in 98% yields. Similarly, chitosan also promoted the curdensation of furfural with 2 effectively to afford 99% yield. Then, phenylbenzaldel. de was reacted with 2 and observed 24% yield of the corresponding product. On ou. r hand, cinnamaldehyde and 2 provided their corresponding condensation product in 64% yield under similar conditions. Interestingly, a bulkier substrate with larger a rension than 1 also effectively reacted with 2 using chitosan catalyst under identical conditions. A similar behavior was also noticed with as 1-naphthaldehyde to provide 93% yield of respective condensation product. Finally, 9-anthracenealdehyde was reacted with 2 to give respective condensation product in 63% yield. This lower activity may be due to the steric nature of the substrate compared to 1naphthaldehyde and 1.

Table 2. Knoevenagel condensation between different aldehydes and **2** in the presence of chitosan as catalyst.^a

Entr	y	Substrate	Product	Yield ^b (%)
1		0	CN CN	97

2	H ₃ C	H ₃ C CN	95
3	H ₃ CO	H ₃ CO CONH ₂	96
4		CN CN	89
5	О	CONH ₂ CN OH	53
6	O ₂ N O	O ₂ N CL. 'H ₂	98
7	Br	Br CONH2	98
8		CONH ₂ CN	99
9		CONH ₂ CN	24
10	O.	CN CONH ₂	64
11	HO CH ₂ CH ₃	HO CN OCH ₂ CH ₃	97
12		CONH ₂ CN	93
13		CONH ₂ CN	63

^aReaction conditions: aldehyde (0.5 mmol), 2 (0.6 mmol), chitosan (20 mg), ethanol:water (0.4 mL), 70 °C, 4 h;

^bYields were determined by GC.

4. Conclusions

In summary, chitosan was shown to be an efficient heterogeneous solid base catalyst for the promotion of Knoevenagel condensation reaction between **1** and **2** to afford high yield of the desired product under mild reaction conditions. As commented earlier, this reaction has not been reported either with homogeneous or heterogeneous catalysts, thus it provides a very simple strategy to obtain condensation product bearing two different functional groups which further can be modified to reach target products. Chitosan enjoys stability under the present experimental conditions and the catalytic activity remains identical up to five cycles with no decay in its performance. Further, powder XRD, FT in, SEM and elemental analyses indicated that the structural integrity and morphology remains almost similar, but in any case, the minor changes in the structure did not affect the caralytic performance. Chitosan has also shown wide substrate scope leading to the formation of large number of condensation products.

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Conflicts of Interest

There are no conflicts to declare

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Graphical Abstract



High stability of catalyst Reusable four times Wide substrate scope

Provide and a second

CRediT author statement

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Declaration of interests

x The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- Chitosan is used as solid base for Knoevenagel condensation reaction
- Catalyst enjoys high stability under the reaction conditions
- Direct synthesis of condensation products is reported
- Catalyst is used for five cycles with no loss in its activity