Application of chitosan-based magnetic organic-inorganic hybrid nanocatalyst for the multicomponent synthesis of α-aminonitriles

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Abstract

In this work, copper ferrite coated chitosan was used as hybrid catalyst for the synthesis of α-amino nitriles by strecker reaction using arylaldehyde, triemethylsilyl cyanide and aromatic amines at room temperature in ethanol as a green solvent. The catalyst was recovered at least five cycles with no significant loss of catalytic activity. Products were isolated easily without need to column chromatography. Good to excellent yields obtained by this method.

Keywords: Nanocatalyst, green chemistry, MCRs, α-aminonitriles.

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1. Introduction

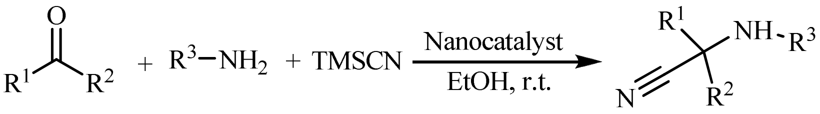
Catalyst has a noteworthy role in chemical processes in both industrial and scientific fields. Use of catalyst can helps to serve less energy, time and money. As a result, chemical process became more eco-friendly and economical. Nanocatalysts are an important branch in this issue[1].

Multicomponent reactions (MCRs) are one of the most effective strategy in the field of green chemistry; witch is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture, and application of chemical products[2]. Therefore, by application of nanocatalysts in MCRs, chemical synthesis can approach aims of green and sustainable chemistry.

As it is mentioned nanocatalyst, are important field and have many advantages in recent years. Magnetic nanocatalysts are a subdivision of catalyst and beneficial strategy in green chemistry. Biocatalysts are another one either. Meet of these two branches results a new, efficient and green nanocatalyst. Chitosan is a biopolymer and it is used in many organic synthesis as catalyst, supporting this with a magnetic nanocatalyst modify this biocatalyst and enhance its properties, also leads to another efficient and green catalyst. α-amino nitriles are an interesting and useful class of intermediates for the synthesis of α-amino acids, various nitrogen-containing heterocycles, amides, and diamines[3,4].

The Strecker reaction between an aldehyde, an amine and hydrogen cyanide is widely regarded as the first multicomponent reactions (MCRs) in organic chemistry and it is the oldest known synthesis of α-amino nitriles that for the first time was reported by Strecker in 1850[5]. This reaction is one of the most direct and efficient methods for the synthesis of α-amino nitriles. The resulting α-amino nitriles are very useful precursors for the synthesis of α-amino acids[6,7] and nitrogen containing heterocycles such as thiadiazoles and imidazoles[8,9] and other biologically useful molecules.[10]

In continuation of our interest in the application of new catalysts in organic synthesis via MCRs[11], herein, efficient and selective syntheses of α-amino nitrile derivatives were carried out using different aromatic aldehydes with amines and trimethylsilyl cyanides in the presence of a catalytic amount of magnetically recoverable chitosan supported magnetic nanoparticles in ethanol at ambient temperature in high yields (Scheme 1). The nanocatalyst can be recovered easily and reused without any significant loss of the catalytic activity.



Scheme1. Magnetic organic-inorganic hybrid nanocatalyst for Strecker reaction.

2. Experimental

2.1. General

All the solvents, chemicals and reagents were purchased from Merck, Fluka and Aldrich. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-470 spectrometer by the method of KBr pellet.

2.2. General procedure for the synthesis of 2-(N-anilino)-2-(4-chlorophenyl)acetonitrile **4a**:

A mixture of 4-chlorobenzaldehyde (0.140 g, 1 mmol), aniline (0.093 g, 1 mmol) and TMSCN (0.120 g, 1.2 mmol) in 3 ml of EtOH was stirred for 15 min at ambient temperature in the presence of the nanocatalyst (0.020 g). After completion of the reaction, as indicated by TLC (ethyl acetate–n-hexane, 1:3), the catalyst was removed easily by adsorbing on to the magnetic stirring bar when the stirring was stopped. Then, the resulted solution was filtered off and the filtrate was evaporated under reduced pressure to afford a pure product. Further purification was followed by crystallization from ethanol to give pure product as pale yellow crystals.

3. Results and discussion

In this work, α-amino nitriles derivatives were synthesized by the reaction of different aromatic aldehydes with aniline and trimethylsilyl cyanides in the presence of a catalytic amount of magnetically recoverable chitosan supported nanoparticles in ethanol at ambient temperature. The results are reported in Table 1. The work up procedure of the product was easy as the nanocatalyst can be separated simply by an external magnet.

Table 1. Synthesis of α-aminonitriles using $CuFe_2O_4$/chitosan nanocatalyst at room temperature.

Entry	**R^1**	**R^2**	**R^3**	**Product**	**Time (min)**	**Yield (%)^a**	**Mp (°C)**	
							Observed	**Litereture**
1	4-Chlorophenyl	H	Phenyl	**4a**	15	94	111-112	108-110[12]
2	4-Bromophenyl	H	Phenyl	**4b**	15	94	100-101	101-103[13]
3	phenyl	H	Phenyl	**4c**	15	85	73-75	75-76 [12]
4	4-Methoxylphenyl	H	Phenyl	**4d**	15	91	90-91	92-94[14]

^{a} Isolated yield

The possibility of recycling the catalyst was examined for several times under optimized conditions. It has been shown that could be recovered and reused several times in the subsequent runs using the same recovered catalyst without a considerable loss of catalytic activity.

4. Conclusions

In summary, we have introduced copperferitte coated chitosan as a magnetic organic-inorganic hybrid nanocatalyst for the multicomponent synthesis of organic compounds. Then, efficient and selective syntheses of α-amino nitrile derivatives were carried out using different aromatic aldehydes with amines and trimethylsilyl cyanides in the presence of a catalytic amount of magnetically recoverable chitosan supported magnetic nanoparticles in ethanol at ambient temperature in high yields.

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