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Research Article

Synthesis of Nano-Maghemite supported coconut chaff catalyst for Mannich reaction

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ABSTRACT

A new bio-friendly catalyst was synthesized *via* impregnation of coconut chaff. Maghemite-coconut chaff (MCC) showed an excellent capability for catalyzing the Mannich reaction in the water as a clean solvent. MCC was easily separated from the reaction medium with a magnet due to its ideal magnetic activities. Moreover, the catalyst showed an outstanding recyclability potential. While the catalyst structure and its properties were investigated by XRD, SEM, and VSM, organic products were fully identified by IR, CNMR, and HNMR.

Keywords: Fe_2O_3; Coconut chaff; Mannich reaction.

1. Introduction

Nanoparticles are proving to be incredibly useful for a wide range of applications, including catalysis. One of the major advantages of using nanoparticles is that they are relatively nontoxic and efficient, making them a great choice for use in natural-product synthesis, organic reactions, pharmaceuticals, and medicinal chemistry. The shape, size, composition, and surface modification of nanoparticles all play a role in their reactivity and toxicity in catalytic systems.

Magnetically recoverable nanocatalysts are particularly effective in chemical transformations because they provide a larger surface area for organic groups to be anchored to. This leads to a decrease in reaction time, an increase in reaction output, and an improvement in the atom economy of the chemical reactions. Additionally, magnetic nanocatalysts are a greener approach towards chemical transformations and can be easily recovered and reused with the help of an external magnet. The most common polymorphs of ferrite structure are "alpha" (hematite) and cubic spinel structure "gamma" (maghemite), both of which can be found in nature.

Generating small-molecule through multicomponent reactions has gained popularity due to their efficiency and speed. These reactions allow for the creation of complex structures using three or more reactants, resulting in the synthesis of target compounds with improved efficiency and atom economy. Interestingly, multicomponent reactions date back to the mid-1800s when α-aminonitriles were first produced by condensing aldehydes with ammonia and hydrogen cyanide, as studied by Strecker. Nowadays, both chemists and the pharmaceutical academics use multicomponent reactions to create structurally complex substances that can be evaluated as lead compounds in drug discovery and development programs. However, it is important to note that there are still limited numbers of such reactions that can be widely applied to prepare biologically relevant molecular frameworks.

The Mannich reaction is a widely recognized method for synthesizing β-amino carbonyl compounds, which play a crucial role in the production of different nitrogen-containing natural products and pharmaceuticals. It is highly favored for its high atom-economy, and so far, many researchers have attempted to enhance and adapt the reaction through various synthetic routes and catalytic systems [1-5].

Herein, we report fabrication of nano γ-Fe_2O_3-Coconut chaff using impregnation method, and its successful utilization as a catalyst in the Mannich reaction.

2. Experimental

2.1. Materials and Characterization

Coconut chaff was purchased from stores near Université de Nantes. All reagents and solvents were purchased from commercial suppliers and used as received without any purifications. X-ray powder diffraction (XRD) measurement was performed using Shimadzu diffractometer equipped with Cu–Kα radiation (λ=1.5418Å). Particles morphology was investigated using Nova 200 NanoLab field emission scanning electron microscope (FE-SEM). Infrared spectra were measured using FT-IR spectrometer in the range of 400-4000 cm^{-1}. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian UnityPlus 300 spectrometer (299.95 MHz for ^{1}H, 75.43 MHz for ^{13}C) at 28 °C.

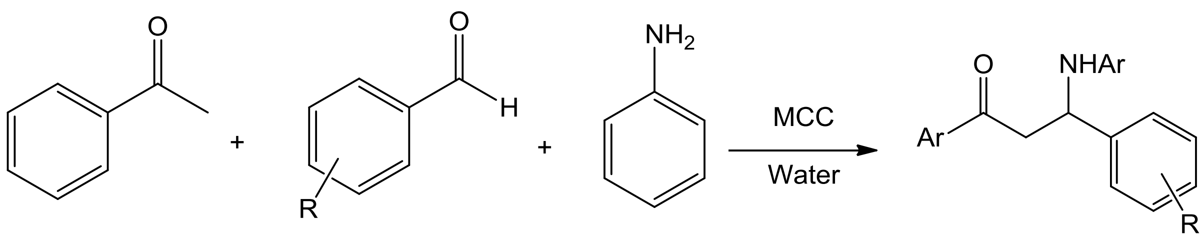
2.2. Catalyst preparation

After soaking the coconut chaff in distilled water and washing it thoroughly until the pH of its solution reached about 7.0, it was dried in an oven at 120 °C for 3 hours to eliminate any remaining moisture. Next, the dried coconut chaff was sifted through a 0.5mm mesh to obtain the fine powder required for the Maghemite supported coconut chaff catalyst's formulation. To prepare the catalyst, Maghemite, which synthesized beforehand based on the reported literature, and the coconut chaff were mixed *via* incipient wet impregnation in a 1:2

proportion based on mass. The mixtures were then dissolved in distilled water and vigorously stirred on a magnetic stirrer for 2 hours. The wet mixtures were heated up to 125 °C in an oven for 24 hours to dehydrate the sample, and finally, the dried sample was calcined at 900 °C for 4 hours in a furnace. The obtained powder named MCC.

2.3. Mannich Reaction

The catalytic behavior of MCC in the Mannich reaction was examined (Scheme 1.) by stirring benzaldehyde (1 mmol), aniline (1 mmol), and acetophenone (1 mmol) in water (5 ml) at room temperature in the presence of 0.1 g catalyst for 2 h. The reaction yielded a high percentage of b-amino ketone, indicating the efficiency of the catalytic system. Catalyst was easily removed with a magnet from the reaction.



Scheme 1. Mannich reaction in the presence of MCC.

3. Results and discussion

3.1. Catalytic evaluation

To assess the catalytic performance of MCC, the reaction of benzaldehyde (1 mmol), aniline (1 mmol), and acetophenone (1 mmol) was carried out. A controlled experiment was conducted in the absence of a catalyst, but the reaction did not proceed and the substrate remained unchanged. Different solvents were also screened, and water was found to be the best medium for the reaction based on the yield and reaction time. Various catalyst loadings were tested, and the best result was obtained with 0.1 g catalyst (Table 1). To explore the scope of the reaction, various derivatives were used as starting compounds, and the results are provided in the Table 2.

Table 1. Initial solvent effect and catalyst loadings studies.

Entry	Solvent	Catalyst loading (g)	Time (hr)	Yield (%)
1	CH_2Cl_2	0.1	2	73
2	CH_3CN	0.1	2	<30
3	EtOH	0.1	2	51
4	MeOH	0.1	2	66
5	Solvent-free	0.1	2	<30
6	**H_2O**	**0.1**	**2**	**90**
7	H_2O	0.2	2	92
8	H_2O	0.5	2	80
9	H_2O	0	2	-

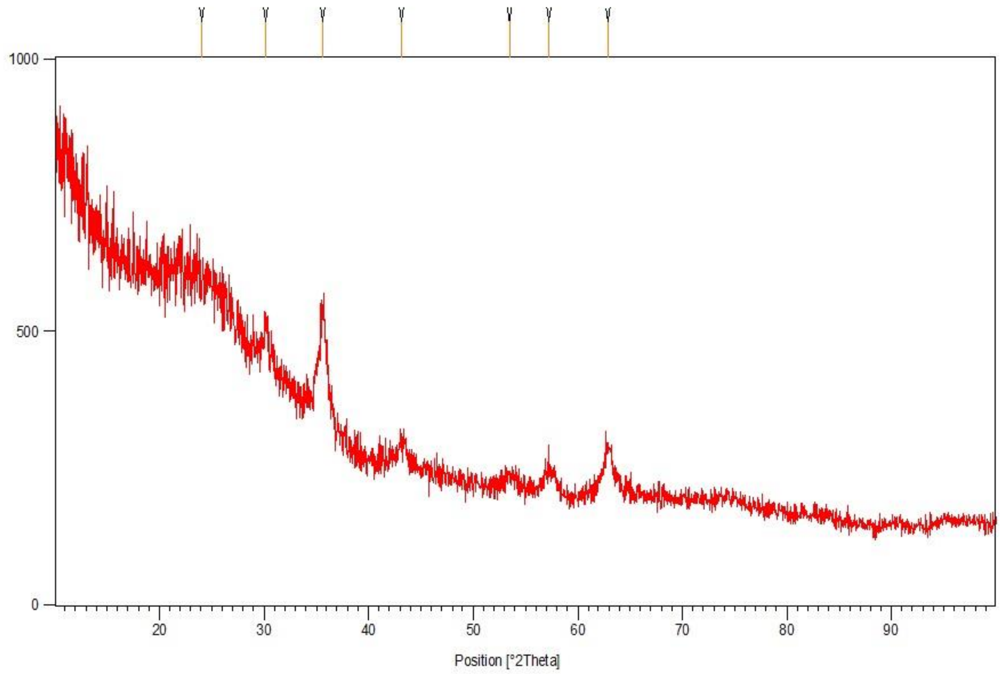
Table 2. Mannich reaction in the presence of MCC.

Entry	R	Product	Yield (%)
1	H	**4a**	90
2	4-Me-C_6H_4	**4b**	91
3	4-Cl-C_6H_4	**4c**	94
4	4-NMe_2-C_6H_4	**4d**	94
5	2- Fluorenyl	**4e**	95
6	4-OMe-C_6H_4	**4f**	91
7	4-Br-C_6H_4	**4g**	96
8	2-Thiophen	**4h**	93

Moreover, as a green catalytic system, the recyclability of the MCC catalyst was investigated by consecutively recovering and then reusing it up to five times. After completion of each cycle the catalyst was washed wish dichloromethane and separated with an external magnet force. The result showed that the catalyst can still retain its high performance without losing any noticeable catalytic effect.

3.2. Catalyst Characterization

The quality and crystallite structural ordering of catalyst were identified by powder X-ray diffraction. Fig. 1 shows wide-angle XRD patterns of MCC catalyst. XRD analysis of catalyst shows Maghemite phase of ferrite oxide without any impurities. All the signals were identified and matched their correspondent standard JCPDS cards.



FE-SEM image illustrates a rough surface with spherical shape and particle size of approximately 30 nm. Meanwhile, VSM analysis confirmed the magnetic activities of the catalyst; based on the result of VSM, MCC exhibits soft-ferromagnetic behavior, meaning it can easily be separated by a magnet from the reaction. MCC catalyst also displayed a relatively high surface area of 125 m^2/g which was derived from BET method of Argon-sorption analysis.

4. Conclusions

This paper reports a successful fabrication of magnetically active nano-Maghemite-coconut chaff (MCC). MCC was utilized as a magnetically enhanced Lewis Acid with relatively decent surface area in Mannich reaction to synthesize the final products with high yield. The reaction was carried out in water as the cleanest solvent available. Magnetic behavior of the catalyst paved the path for a simple and environmentally friendly reaction.

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