

Nano $\text{MgCuAl}_2\text{O}_5$: Synthesis by Sol-Gel Auto-Combustion Process, Characterization and Reusable Heterogeneous Catalyst for the Hantzsch 1,4-Dihydropyridine Reaction

Marzieh Mahmoodi Keshtiban,¹ Abbas Nikoo^{2,*} and Bakhshali Massoumi^{1,*}

¹ Department of Chemistry, Payame Noor University, Tehran, Iran

² Department of Organic Chemistry, Faculty of chemistry, Urmia University, Urmia, Iran

* Corresponding author: E-mail: b_massoumi@pnu.ac.ir
a.nikoo@urmia.ac.ir

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Abstract

For the first time, $\text{MgCuAl}_2\text{O}_5$ heterogeneous nanocatalysts were prepared by sol-gel auto-combustion method, which displayed great yield and suitable activity for the preparation of 1,4-DHP derivatives with high efficiency in green solvent ethanol/water (1:1) at 80 °C under one pot condition. The synthesis materials were separated in short reaction times with excellent yield (80–95) %. Moreover, the synthesized nanocatalyst was easily retrieved and continuously reused for six reactions without a noticeable significant loss of proficiency. The solid catalyst was confirmed by XRD, BET, FTIR, FESEM and EDX, and the substituted 1,4-dihydropyridines were characterized by melting point, ¹H and ¹³C NMR.

Keywords: Heterogeneous catalyst, Sol-Gel auto-combustion, Recyclable, One-pot synthesis, 1,4-Dihydropyridine.

1. Introduction

In modern synthetic organic chemistry, one-pot Multi-component reactions (MCR) are a powerful synthetic tool that produces complex heterocyclic molecules and pharmaceutical compounds they have many advantages over classical multistep reactions, including easy handling and efficiency, no need for excess separation steps and economy of materials, energy and time.^{1–3}

In the path of achieving green chemistry, the synthesis process of organic compounds has undergone changes in recent decades. It is progressing towards being environmentally friendly, although laboratory research for the innovation of new methods is expanding consequently.⁴ The design and development of new synthetic methods that do not have a negative impact on humans and the environment, as well as the recycling of materials, are among the goals of green chemistry.^{5,6} The usage of heterogeneous catalysts in one-pot conditions is one of the important factors for achieving green chemistry.⁷

Heterogeneous nanocatalysts have attracted attention in the past years in various chemical industries and research centers due to their properties such as selectivity, activity and stability. The most obvious feature is easy recycling,

which is confirmed by the exponential increase in the number of patents and technologies.^{8–10}

Arthur Rudolf Hantzsch opened a new horizon in the synthesis of drugs by synthesizing 1,4-dihydropyridine compounds, which are useful and effective antiviral,¹¹ antidepressant,¹² anti-inflammatory,¹³ anti-mutagenic,¹⁴ anti-diabetic,¹⁵ anti-hypertensive,¹⁶ sedative,¹⁷ vasodilator,¹⁸ and antibacterial¹⁹ drugs, research to improve and modify Hantzsch's method by organic chemists is expanding.

Several methods with various catalysts and in the different reaction conditions for the synthesis of 1,4-dihydropyridine have been reported in scientific research articles such as ZnFe_2O_4 ,²⁰ $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Zn}_y\text{O}_3$,²¹ $\text{Fe}_3\text{O}_4@ \text{Co}(\text{BDC})\text{NH}_2$,²² $\text{Fe}_2\text{O}_3/\text{ZrO}_2$,²³ $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{ADMPT}/\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$,²⁴ Sulphated Tin Oxide,²⁵ Fe_3O_4 supported glutathione,²⁶ sulphated poly borate,²⁷ DBU,²⁸ SBA-DAB-CO,²⁹ SiO_2 ,³⁰ trimethylamine,³¹ Fe-CuZSM-5,³² $\text{CoFe}_2\text{O}_4@ \text{SiO}_2\text{-NH}_2\text{-CoII}$ ³³ and graphene oxide/Cu NPs.³⁴ However, many reported methods suffer from long reaction times, low efficiencies, moisture sensitivity, difficult synthesis processes, as well as expensive materials used and non-recyclable catalysts.³⁵

In this research, $\text{MgCuAl}_2\text{O}_5$ heterogeneous nanocatalyst was synthesized for the first time by sol-gel au-

to-combustion method with a simple, cheap and non-toxic preparation method. This solid nanocatalyst does not lose its effect in the long term and is stable and does not deteriorate under the influence of heat, air and moisture. Next, by one-pot reaction, 1,4-DHP derivatives were prepared in green solvent ethanol/water (1:1) with high efficiency and short duration. It is worth noting that the catalytic property was maintained in six consecutive reactions, and the $\text{MgCuAl}_2\text{O}_5$ nanocatalyst can be separated after the end of the reaction and reused.

2. Experimental Section

2.1. Materials

Ethyl acetoacetate, Urea, Ammonium acetate, $\text{Mg}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Aldehyde derivatives, and the solvents were used during the reaction were purchased from reputable companies such as Merck and Sigma-Aldrich, which were used without the need for purification. D500 diffractometer (Siemens) was employed for the pattern X-ray diffraction (XRD) of the $\text{MgCuAl}_2\text{O}_5$ heterogeneous nanocatalysts at 25 °C using Cu K α radiation ($\lambda = 0.154$ nm) in a scanning rate of 2° per min, at 40 kV. Data have been collected with a step size of 0.05° degrees and a temperature range of 10–80°, nominal time per step of 1 s, and slit width of 5 nm to confirm the type of structure and check the purity of synthesized nanoparticles. Information about the morphology and size of the $\text{MgCuAl}_2\text{O}_5$ heterogeneous nanocatalysts was obtained with the device field emission scanning electron microscopy (FESEM, TESCAN MIRA III) with 20 kV accelerating voltage. X-ray electron dispersive spectroscopy (EDX) using a SAMX detector has been employed to analyze and specify the relative abundance of elements. Spectroscopy Fourier transforms infrared (FTIR) was used on a Thermo AVATAR spectrometer in the range of 4000–400 cm^{-1} with a KBr disk. Specific BET surface area (SBET) amounts were computed with $0.05 < P/P_0 < 0.30$. The total pore volume (V_t) was estimated from the adsorption data at a P/P_0 value of 0.99. To determine the porosity of the catalyst surface, spectroscopy BET in a Micrometrics Gemini surface area analyzer was used under liquid nitrogen. Catalyst capacity was specified by atomic absorption method with BEL SORP MINI II absorption appliance. Low-temperature N_2 adsorption–desorption isotherms of the $\text{MgCuAl}_2\text{O}_5$ heterogeneous nanocatalysts were obtained on a BEL PREP VAC II analyzer. The $\text{MgCuAl}_2\text{O}_5$ heterogeneous nanocatalysts were outgassed at 450 °C overnight Prior to N_2 adsorption. The multipoint Brunauer–Emmett–Teller (BET) method was operated for the total specific surface area. Continuously, the progress process of the reaction was prosecuted by TLC plates (silica-gel PolyGram SILG/UV254) and relevant tests. Finally, the reaction completion time was determined. By using different equipment and spectroscopic techniques, the obtained

products were identified. Melting points were recorded by open capillary on Electrothermal 9200, and contrasted with reference models. ^1H and ^{13}C spectra were registered with a Bruker Avance-300 MHz spectrometer. Chemical shifts were described in ppm using TMS as an internal standard, and CDCl_3 was used as solvent at room temperature. All yields mention separate products.

2.2. Synthesis of $\text{MgCuAl}_2\text{O}_5$ NPs

A sol–gel auto-combustion method with a ratio of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (25 mmol), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (50 mmol), and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (25 mmol) at the presence of Urea as a fuel for the synthesis of $\text{MgCuAl}_2\text{O}_5$ NPs was applied. In 1000 ml distilled water, 6.40 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 18.75 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 6.05 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were dissolved. 25 g of Urea was dissolved in 250 ml of distilled water then added to the mixture, and stirred for 3 h. The formation of a gel happened by evaporation of the solution. The obtained gel was heated at 80 °C overnight by an oven and calcined at 750 °C for 4 h in air.

2.3. Preparation of 1,4-Dihydropyridines

Considering the time required for each reaction, a mixture of aryl aldehyde (2.5 mmol), NH_4OAc (3.75 mmol), ethyl acetoacetate (5 mmol) and $\text{MgCuAl}_2\text{O}_5$ nanocatalyst (37.5 mg) in ethanol/water (1:1) was heated under 80 °C. After the completion of the reaction, as monitored by TLC (ethyl acetate/petroleum ether 1:3), the reaction temperature was down to 25 °C, and 25 mL of water was added to the reaction mixture. The catalyst was detached for use in the next reaction by ordinary centrifugation. The 1,4-DHP derivatives were extracted with ethyl acetate (3×25 mL), and the organic layer was dried with anhydrous Na_2SO_4 (50 g). Ethyl acetate was separated from the product under reduced pressure, and 1,4-DHP derivatives with 80–95% yields were afforded by recrystallization of residue from ethanol.

3. Results and Discussion

3.1. Characterization

The structural property of $\text{MgCuAl}_2\text{O}_5$ NPs was analyzed by powder XRD (Figure 1). X-Ray diffraction pattern of $\text{MgCuAl}_2\text{O}_5$ NPs proved that the presence of only phase with $2\theta = 31.5, 35.6, 37.0, 38.8, 45.0, 49.0, 59.5$ and 65.5 after calcination at 750 °C. The data was analyzed in the 2θ degree range from 10° to 80° with the scanning step of 0.5 per sec. The XRD pattern is the replica of the JCPDS pattern with reference code 96-901-6435. This indicates the formation of single-phase pure cubic $\text{MgCuAl}_2\text{O}_5$ NPs crystallites. The crystal size of $\text{MgCuAl}_2\text{O}_5$ NPs was computed with the Debye Scherrer equation ($\text{Particle Size} = 0.9 \times \lambda / d \cos \theta$), where $\lambda = 1.54060$ Å (in the case of Cu K α),

d = the full width at half maximum intensity of the peak in radian and θ is the Bragg's angle in degree. The particle size of $\text{MgCuAl}_2\text{O}_5$ NPs was calculated to be about 43 nm.

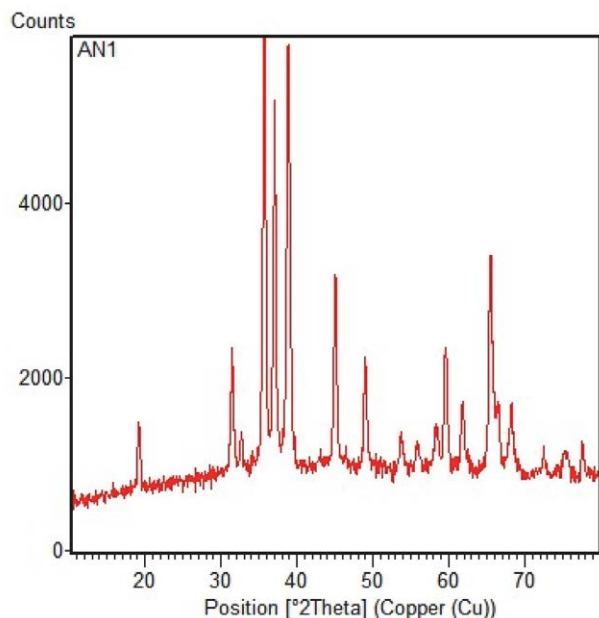


Figure 1. XRD pattern of $\text{MgCuAl}_2\text{O}_5$ NPs

By scanning electron microscopy, the size distribution, surface morphology of this particle and particle shape were investigated (FESEM; Figure 2), which showed the nanostructure of $\text{MgCuAl}_2\text{O}_5$ NPs. The FESEM picture

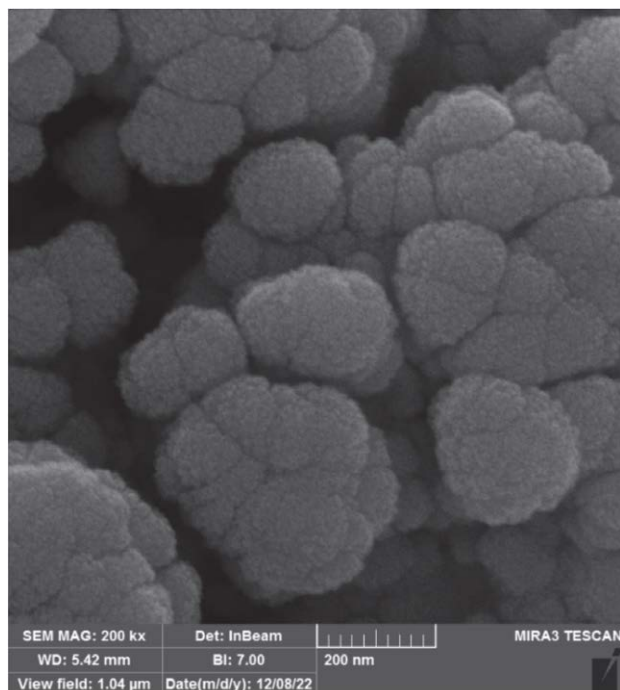


Figure 2. FESEM images of $\text{MgCuAl}_2\text{O}_5$ NPs

shows that the average size of $\text{MgCuAl}_2\text{O}_5$ is about 43 nm, which is thoroughly consistent with the XRD pattern and the number obtained from the Debye-Scherr formula. The state of aggregation of $\text{MgCuAl}_2\text{O}_5$ NPs shows that the materials are crystalline and homogeneous, which indicates the dominance of active sites and the effectiveness of catalyst becoming more.

The stoichiometry and chemical purity of the $\text{MgCuAl}_2\text{O}_5$ NPs were checked by energy dispersive X-ray spectroscopy (EDX) studies. The elemental composition of nanoparticles is O, Mg, Cu and Al, which was determined by the EDX spectrum as the just main ingredients of $\text{MgCuAl}_2\text{O}_5$ (Figure 3).

Figure 4. shows the Fourier transform infrared (FT-IR) spectrum of $\text{MgCuAl}_2\text{O}_5$ NPs. In this spectrum, the

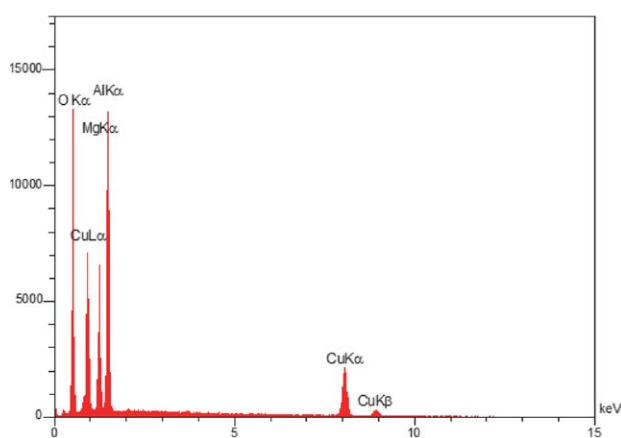
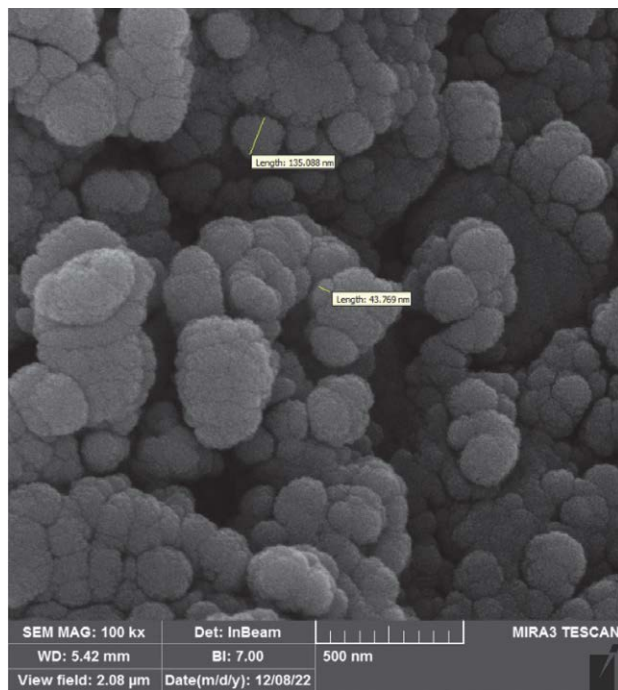


Figure 3. EDX spectrum of $\text{MgCuAl}_2\text{O}_5$ NPs



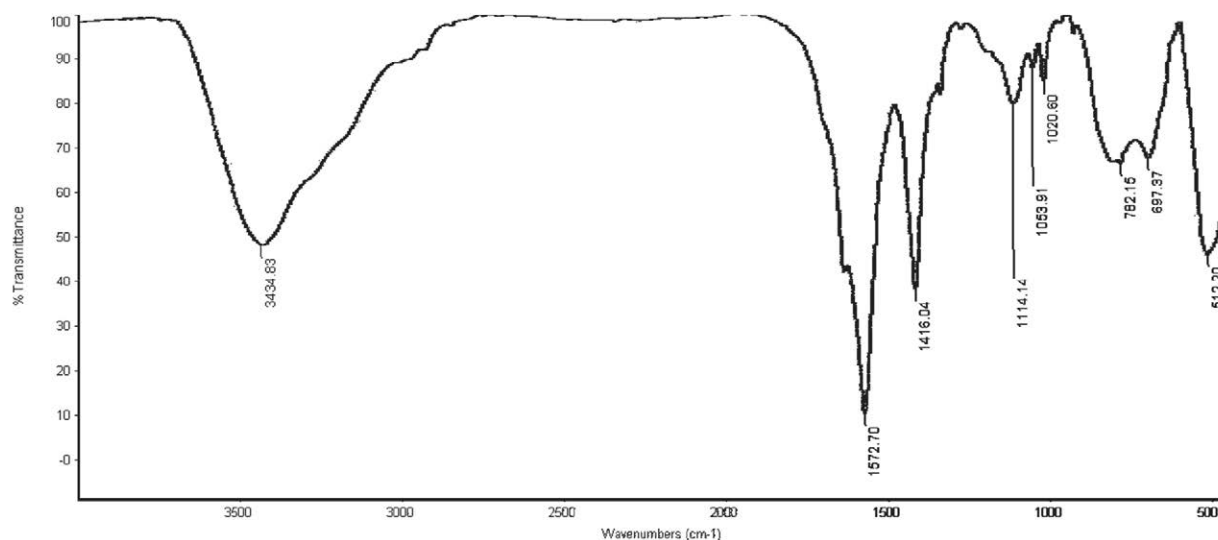


Figure 4. FT-IR spectrum of $\text{MgCuAl}_2\text{O}_5$ NPs

wide peak that emerged in the confine of 3434 cm^{-1} is related to the stretching disposition of the absorbed water. The stretching vibration of the Al–O band is in 1572 cm^{-1} , while the bending vibration is at 782 cm^{-1} . 1416 and 697 cm^{-1} are respectively related to the stretching and bending vibrations of the Mg–O band. The stretching vibration of the Cu–O is 1114 cm^{-1} , and the bending vibration of it is 512 cm^{-1} .

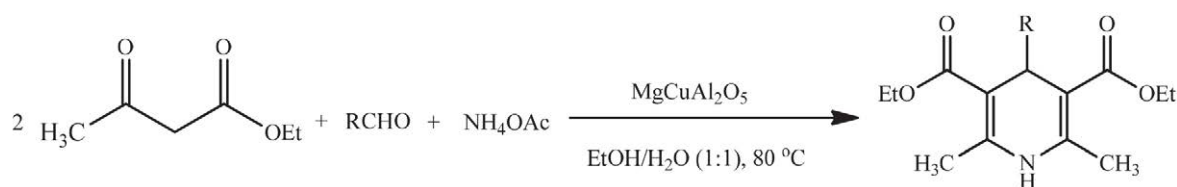
Figure 5. shown the N_2 adsorption-desorption isotherm of the $\text{MgCuAl}_2\text{O}_5$ NPs. N_2 adsorption-desorption isotherms were used to measure the size distribution, specific surface area and pore volume of $\text{MgCuAl}_2\text{O}_5$ NPs at 77 K (ASAP 2010 Micromeritics). The pore size distribution and pore volume were computed by using the BJH method, and the surface area was computed by using the BET equation. In order to evacuate the physisorbed moisture, before the BET test, the $\text{MgCuAl}_2\text{O}_5$ nanocatalyst was degassed at 120 °C for 4 h under vacuum. The type IV absorption isotherm (range 2 P/Po 0.990) affirmed the nature of the sample, which was mesoporous. The surface area of the catalyst was $6.3636\text{ m}^2\text{ g}^{-1}$, and the pore size of 252.31 Å with a pore volume of $0.040139\text{ cm}^3\text{ g}^{-1}$.

3. 2. Catalytic Activity

In the present work, $20\text{ mol\%}$ of $\text{MgCuAl}_2\text{O}_5$ NPs was used throughout the experiments. 2.5 mmol of differ-

ent aromatic aldehydes and 3.75 mmol ammonium acetate with 5 mmol of ethyl acetoacetate were stirred at 80 °C in the presence of $\text{MgCuAl}_2\text{O}_5$ nanocatalyst to produce the 1,4-DHP derivatives in excellent yield (Scheme 1). The reaction progress was regularly checked by TLC plates and observed by UV (254 nm) light. After completion of the reaction, the 1,4-DHP derivatives were extracted by ethyl acetate.

In continuation of this research, to select the appropriate solvent, water and ethanol/water (1:1) were used in the model reaction in the presence of $\text{MgCuAl}_2\text{O}_5$ nanocatalyst at 80 °C . As said in Table 1, we found that ethanol/water (1:1) is the most efficient solvent for synthesizing 1,4-DHP derivatives, due to the hydrophobicity of the catalyst and organic reactant materials, giving the product in 90% yield (Table 1, entry 3). In the early stages without a catalyst, no product was synthesized in the reaction mixture even after stirring for 60 minutes . In order to achieve the desired product with the best yield, the reaction was optimized by using different amounts of catalyst (18.75 , 37.5 and 56.25 mg). For each of these quantities, the yields were 75 , 90 and 89% , respectively. The best efficiency was obtained with 37.5 mg of catalyst at 80 °C in ethanol/water solvent with a ratio of 1:1 (Table 1). After stirring the reaction mixture for 60 minutes , the yield increased to 90% , which is a great improvement. In fact, by increasing the quantity of catalyst from 18.75 to 37.5 mg , the yield raised



Scheme 1. Synthesis of 1,4-DHP derivatives

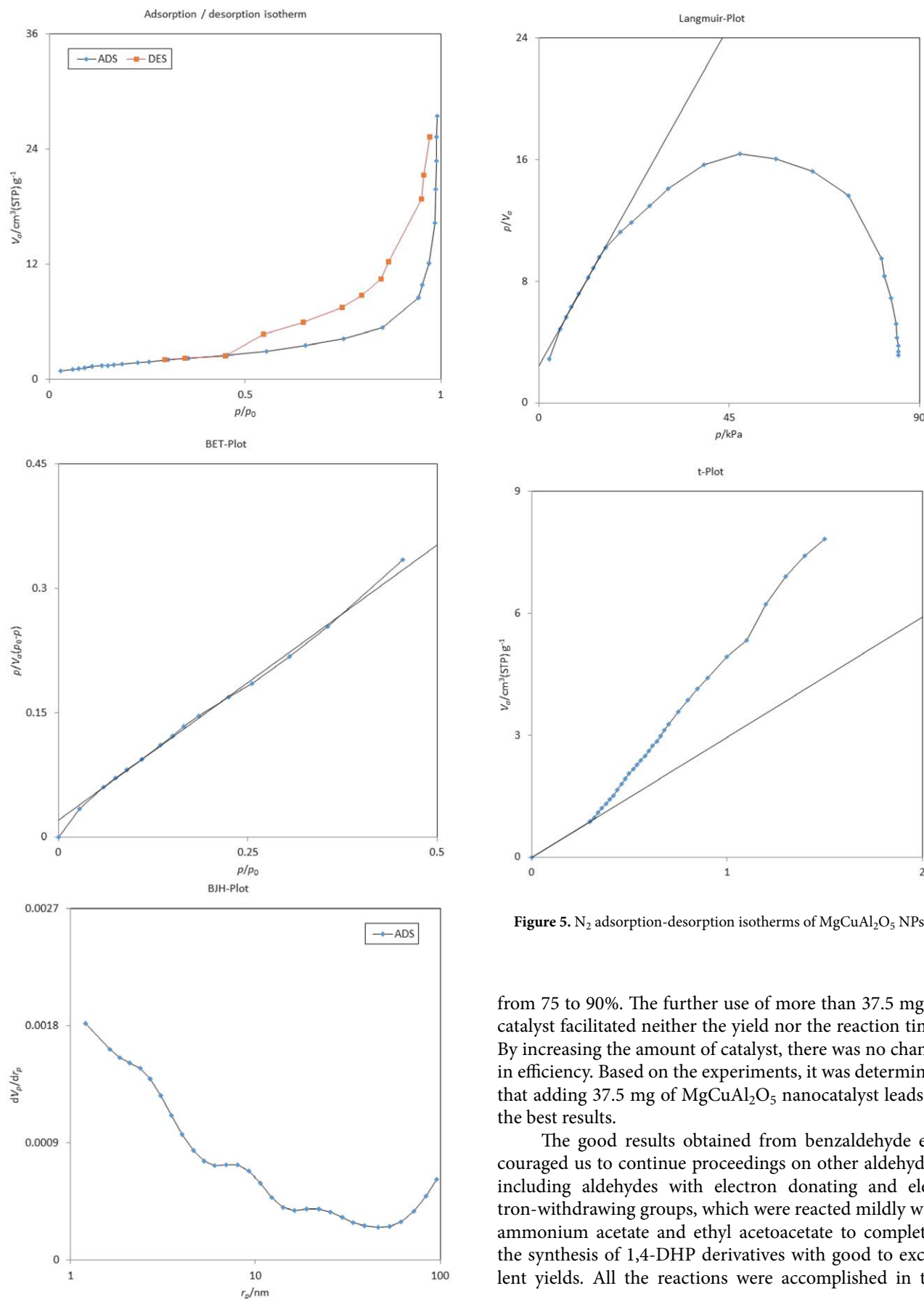


Figure 5. N_2 adsorption-desorption isotherms of $MgCuAl_2O_5$ NPs

from 75 to 90%. The further use of more than 37.5 mg of catalyst facilitated neither the yield nor the reaction time. By increasing the amount of catalyst, there was no change in efficiency. Based on the experiments, it was determined that adding 37.5 mg of $MgCuAl_2O_5$ nanocatalyst leads to the best results.

The good results obtained from benzaldehyde encouraged us to continue proceedings on other aldehydes, including aldehydes with electron donating and electron-withdrawing groups, which were reacted mildly with ammonium acetate and ethyl acetoacetate to completed the synthesis of 1,4-DHP derivatives with good to excellent yields. All the reactions were accomplished in the

Table 1. Optimization of $\text{MgCuAl}_2\text{O}_5$ nanocatalyst^a

Entry	Solvent	Catalyst (mol%)	Time (min)	Yields (%)
1	ethanol/ water (1:1)	–	60	Trace
2	ethanol/ water (1:1)	10	60	75
3	ethanol/ water (1:1)	20	60	90
4	ethanol/ water (1:1)	30	60	89
5	water	–	60	Trace
6	water	10	60	18
7	water	20	60	42
8	water	30	60	57

^a 2.5 mmol benzaldehyde, 5 mmol ethyl acetoacetate, 3.75 mmol ammonium acetate under 80 °C

presence of $\text{MgCuAl}_2\text{O}_5$ using in catalytic quantity (20 mol%) in ethanol/water (1:1) at 80 °C. The results of the experiments, which are also mentioned in the table, show

that the yield and the reaction rate changes with the variation of the functional groups on benzaldehyde, so that the electron-withdrawing functional groups lead to an increase in efficiency and the reaction rate. However, the electron-donating functional groups cause a decrease in it. Generally, 45 to 140 mins are needed to complete all the reactions. The synthesis of 1,4-DHP derivatives was obtained in 80–95% yields (Table 2).

Based on what is proposed in various scientific articles for synthesizing 1,4-DHP derivatives, we also present a proposed mechanism (Scheme 2). In the first step, the $\text{MgCuAl}_2\text{O}_5$ nanocatalyst led to the production of ester enamine from β -ketoester. Then, β -ketoester and aryl aldehyde produced chalcone intermediate during aldol condensation in the presence of $\text{MgCuAl}_2\text{O}_5$ nanocatalyst. In the end, ester enamine and chalcone produce 1,4-DHP derivatives with the Michael addition by removing the water.

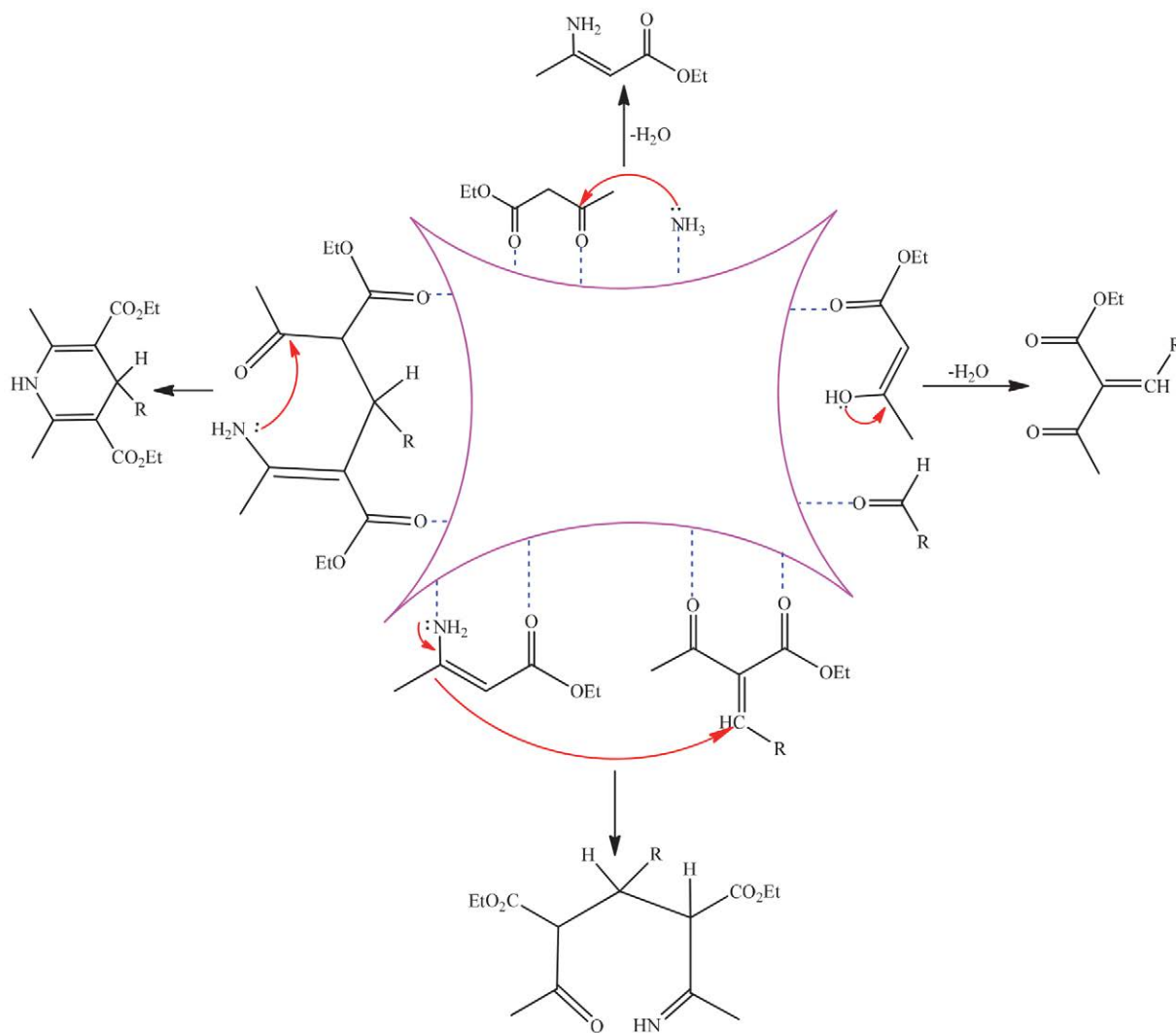
**Scheme 2.** The Suggested mechanism for synthesis of 1,4-DHP derivatives

Table 2. Synthesis of 1,4-DHP derivatives^a

Entry	R	Time (min)	Yield (%)	MP (°C)	
				Found	Reported ^{36–46}
1	3-Me-Ph	110	85	121–123	122–124
2	4-Me-Ph	130	83	135–137	137–139
3	4-MeO-Ph	120	82	161–163	158–160
4	2-HO-Ph	140	80	159–161	162–163
5	3-HO-Ph	100	88	181–183	180–182
6	4-HO-Ph	120	81	228–230	226–228
7	2-O ₂ N-Ph	100	89	119–121	118–120
8	3-O ₂ N-Ph	55	91	166–168	163–165
9	4-O ₂ N-Ph	45	93	126–128	129–131
10	2-Cl-Ph	80	90	143–145	144–145
11	4-Cl-Ph	50	95	155–157	158–161
12	2,4-diCl-Ph	70	89	239–241	241–242

^a 2.5 mmol aldehyde, 5 mmol ethyl acetoacetate, 3.75 mmol ammonium acetate and 37.5 mg of MgCuAl₂O₅ nanocatalyst in ethanol/water (1:1) at 80 °C

3. 3. Reusability of the Catalyst

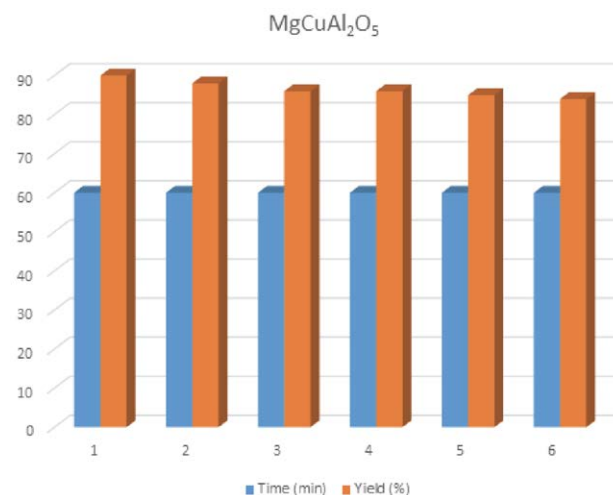
To prove the reusability of the MgCuAl₂O₅ nanocatalyst in the synthesis of 1,4-DHP derivatives, it was tested during optimal reactions. MgCuAl₂O₅ nanocatalyst can catalyze several reactions without significantly loss of its catalytic activity. As will explained in the experimental section, after the end of each reaction, the catalyst, by simple filtration, was recycled for the subsequent reaction. The separated MgCuAl₂O₅ nanocatalyst was washed with water, ethanol and ethyl acetate, dried at 80 °C under vacuum for 2 h, and reused further in the next reaction without further modification. This process was performed over six runs with only a slight reduction in the catalytic activity, showing that all of the reactions were performed at favorable yields. In the specific time, the yield obtained for the reusability of the catalyst can be compared (Table 3), which shows that the recycling and reusability were accomplished without considerable loss of catalytic activity. According to the outcomes, the MgCuAl₂O₅ nanocatalyst showed great stability and excellent activity during several successive re-

Table 3. Reusability of MgCuAl₂O₅ nanocatalyst^a

Entry	Time (min)	Yield (%)
1	60	90
2	60	88
3	60	86
4	60	86
5	60	85
6	60	84

^a 2.5 mmol benzaldehyde, 5 mmol ethyl acetoacetate, 3.75 mmol ammonium acetate and 37.5 mg of MgCuAl₂O₅ nanocatalyst in ethanol/water (1:1) at 80 °C

actions, so that after six consecutive reactions for the preparation of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate, the yield of the catalyst decreased by only 6%. These meager amounts reflect that the MgCuAl₂O₅ nanocatalyst preserves its activity and durability during recycles.

Figure 6. Reusability of MgCuAl₂O₅ nanocatalyst

4. Conclusion

In conclusion, in this article, an efficient and convenient process has been used to prepare various symmetrical 1,4-DHPs from the one-pot reaction of ethyl acetoacetate, different aryl aldehydes, and ammonium acetate using 20 mol% MgCuAl₂O₅ nanocatalyst as a new heterogeneous catalyst at 80 °C in ethanol/water (1:1), which has many privileges such as ease of preparation, insolubility in most organic solvents, being eco-friendly and green process catalysts for green synthesis of 1,4-DHP derivatives in excellent yields. Also, the MgCuAl₂O₅ nanocatalyst could be successfully recovered and recycled at least for six runs without significant loss in activity. The method offers several advantages, including more efficient and economical than previous ones and offers advantages such as fewer reaction times, more yields, an environmentally friendly procedure, easy isolation of catalyst, and simple work-up procedure. The MgCuAl₂O₅ nanocatalyst was identified by XRD, SEM, EDX and FTIR techniques. The structure of 1,4-DHP derivatives has been specified by ¹H and ¹³C NMR.

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Povzetek

Avtorji v prispevku poročajo o pripravi $\text{MgCuAl}_2\text{O}_5$ heterogenega nanokatalizatorja s sol-gel metodo samozgorevanja. Nanokatalizator je pokazal odlično aktivnost in visoko učinkovitost pri enostopenjski sintezi derivatov 1,4-dihidropiridina (1,4-DHP) v zmesi etanol/voda (1:1) kot zelenem topilu pri 80 °C. Reakcije potekajo hitro in z odličnimi izkoristki (80–95%). Poleg tega je nanokatalizator mogoče hitro obnoviti in ponovno uporabiti v najmanj šestih zaporednih ciklih brez znatne izgube aktivnosti. Nanokatalizator je bil karakteriziran z XRD, BET, FTIR, FESEM in EDX, ter temperaturo tališča. Substituirane 1,4-dihidropiridine pa so okarakterizirali z ^1H in ^{13}C NMR spektroskopijo.



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