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Original Research Article

Cerium oxide/alumminium oxide-nanocatalyst promoted the production of dihydropyrano[c]chromene derivatives

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Nanocatalyst
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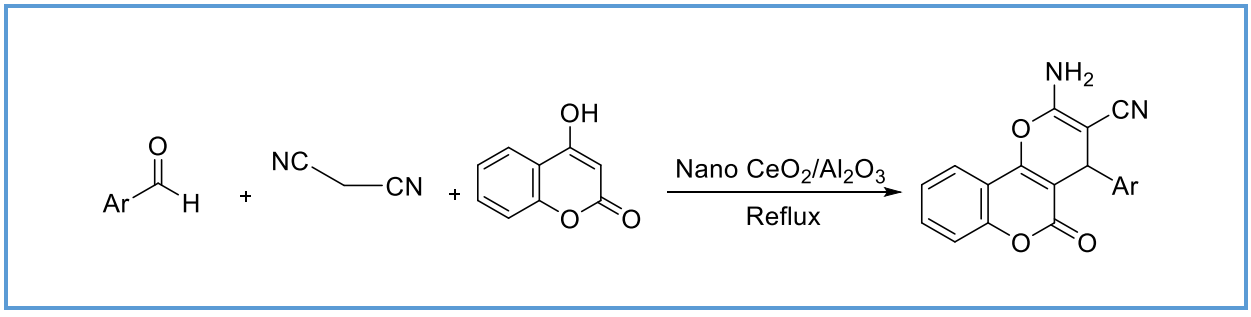
ABSTRACT

Due to various biological and pharmaceutical applications, derivations of Dihydropyrano[c]chromene have received great attention from researchers. Because of the considerable significance of these compounds, various methods with different conditions and catalysts have been used to synthesize them. However, some of these methods have disadvantages such as low efficiency, prolonged reaction time, toxic solvents. In this research, the performance of Cerium oxide/aluminum oxide for synthesizing the derivatives of dihydropyrano (c) chromene as an effective and nonhomogeneous catalyst has been investigated. This method contains numerous advantages, which are discussed in the following.

Graphical Abstract



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Introduction

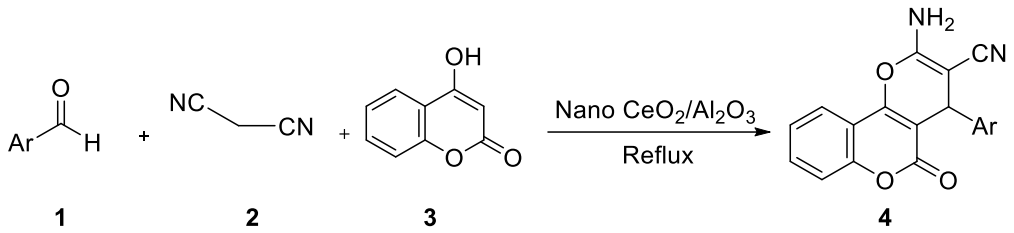
Heterocyclic compounds are widely applied and can be found among herbal, chemical, veterinary, and pharmaceutical compounds. Heterocyclic compounds are used as anti-oxidizing, additive, optical brightener, anticorrosion, and many other factors. One of the most critical features of Heterocyclic compounds is that active groups may appear as the cyclic system or as a substituent. These compounds are also used as the borderlines of organic synthesis. Chromenes known as benzopyrans are essential heterocyclic compounds having Oxygen. These compounds are of excellent synthesis significance due to their high reactionability and biological activities.

Chromenes which are also mentioned as dihydropyrano[c]chromene, are one of the important classes of heterocyclic compounds which the chemists concentrate in recent years due to some biological and pharmaceutical features such as anticoagulant, anti-tumor, anticancer, diuretic, and so on properties [1–4]. Other applications of these compounds include their usage as cognitive enhancers in neural disease remedies such as Alzheimer, Huntington, schizophrenia (dementia praecox), and Parkinson [5]. Chromene derivatives are used as crucial and applied precursors in synthesizing different pharmaceutical and chemical compounds. However, the structural unit of these compounds is also found in natural compounds [6]. According to the vast application of x[c]chromene derivatives. In most preparation methods of dihydropyrano[c]chromene, 4-hydroxoy coumarin, and maslononitrile [7–9].

Various materials have been applied as the catalyst for synthesizing these compounds, among which Hexadecyl dimethyl benzyl ammonium bromide, sodium bromide, fluoride ion, lithium bromide, cesium chloride, sodium selenide, tetrabutylammonium bromide, sodium carbonate, potassium carbonate, porous silica nanoparticles, titanium dioxide nanoparticles, and lipase could be mentioned [9–17]. Nanocatalysts are widely used in chemical processes, energy generation, energy-saving, and preventing environmental pollution. Nowadays, catalytic technologies are converting coal, petroleum, and natural gases to fuels and making different kinds of petrochemical products. Nanocatalysts are used in oil, chemical compound synthesizers, petrochemical industries, the environment, and other industries.

Metal oxides play essential roles in all cases, such as chemistry, physics, and Materials science. Metal elements constitute a large variety of oxides and thus can create many structures. In technological applications, metal oxides are used in sensor production, microelectromechanical circuits, fuel cells, piezoelectric devices, coverings for corrosion deactivation, and catalysts. Cerium nano oxide/aluminum oxide is used in different technological processes such as removing the whole organic carbon from the waste, hydrocarbon oxidations, enhancers, and catalysts [18].

Following the discovery of the medicinal properties of these derivatives in recent years and using nanocatalysts for synthesizing these compounds [19–28], the synthesis of these compounds has been considered. Here we evaluate the synthesis of these compounds using nano-cerium oxide/aluminum oxide as an efficient catalyst (Scheme 1)



Scheme 1. Synthesis of dihydropyrano[*c*]chromene

Experimental

The melting temperatures of the compounds were measured using the KRUSs (KSP-IN 90-264). IR-spectrums of the compounds are measured by the spectrometer FT–IR Tensor 27. The HNMR spectrum was recorded by the spectrometer AVANCE BRUKER DRX 400 MHZ. The solvents and chemicals used in this research were purchased from MERCK Company. The structure of the produced products was compared and affirmed by adapting the spectrum and physical data recorded in the references.

Synthesizing method for dihydropyrano[c]chromene in the presence of nano Cerium oxide/aluminum oxide

In this method, 1 mmol of 4-hydroxy coumarin (0.162 g), 1 mmol malononitrile (0.06 g), 1 mmol aldehyde, 5 mL water, and 0.05 g cerium oxide/aluminum oxide are added to the balloon and refluxed. After the reaction, which was identified by TLC, the reaction mixture was cooled and filtrated. The resulted precipitin is filtrated and recrystallized in ethanol (Table 1).

4c: IR (KBr, cm^{-1}): 3379, 3265, 3153, 2189, 1717, 1677, 1613, 1386, 1067, and 764. ^{1}H NMR (400 MHz, DMSO): δ 4.56 (s, 1H), 7.36 (d, 2H, J = 8.3 Hz, Ar-H), 7.36 (brs, 2H, NH_2), 7.43 (brs, 2H, Ar-H), 7.54 (d, 1H, J = 7.78 Hz, Ar-H), 7.49 (t, 1H, J = 7.78 Hz, Ar-H), 7.75 (dt, 1H, J = 7.26,1.5 Hz, Ar-H), 7.93 (dd, 1H, J = 7.78, Hz, Ar-H).

Result and Discussion

We have established a one-pot reaction of various aldehydes with malononitrile and 4-hdroxy coumarine in water in the presence of nano-CeO_2/Al_2O_3 as an available and green and inexpensive catalyst in good yields for synthesizing dihydropyrano[c]chromene (Table 1). After optimizing the reaction conditions, different aldehydes with electron donating andelectron-withdrawing groups, were investigated for the present protocol. It can be seen from the data that all reactions proceeded were performed well and produced the corresponding products in good yields and in very short reaction times (Table 1).

Preparation of cerium nano oxide/aluminum oxide

The oxidized nanoparticles of the nano cerium oxide/aluminum oxide mixture were synthesized at room temperature using the chemical method. 50 mL of 0.1 M Cerium Nitrate solution and 50 mL of 0.1 M aluminum sulfate are mixed. Then, 100 mL of a 2 M sodium hydroxide solution is added to the above mixture. Then the obtained solution was heated for 3 hours at 80 °C and washed several times with deionized water to remove impurities**.** The resulted product was dried up at room temperature and calcined at 700 °C [29].

The scanning electron microscope (SEM, SU-70, Hitachi) and transmission electron microscope (TEM, TF 20 Tecnai G2 200 kV FEI) images of the catalyst are demonstrated in

Figure 1 and 2. The prepared NCs shape and morphology were studied using TEM analysis.

The presence of Ce, Al, and O is confirmed by elemental analysis with the help of EDAX (Figure 3).

The XRD of CeO_2-Al_2O_3 was represented in Figure 4, which denotes the crystalline phase. The peaks observed at 2θ angle of 22.3, 25.2, 28.8, 37.5, 38.2, 45.9, 52.2, 54.3, 57.3, and 67.5° denotes Al_2O_3 presence. Peaks observed at 2θ angle of 28.1, 32.7, 48.3, 55.8, 58.7, 67.6, and 78.4° denote cubic CeO_2 existence. In the XRD diffractogram of CeO_2-Al_2O_3 indicates the successful preparation of CeO_2-Al_2O_3 NCs (Figure 4).

Catalyst optimization

To obtain the optimal value for the catalyst, different concentrations of the catalyst (0.02, 0.02, 0.05, and 0.1 gr) were used in the evaluated reaction to result in the best efficiency in the proper time from the product. The obtained results are reported in Table 1.

The results from the Table 1 indicate that the efficiency is low in the absence of a catalyst. However, the efficiency is increased while using cerium nano oxide/ aluminum oxide. It could be concluded from Table 2 that the best value for the catalyst is 0.05 g. Therefore, as can be seen from the Table 2, the best amount of catalyst that can be used for the reaction is 0.05 g.

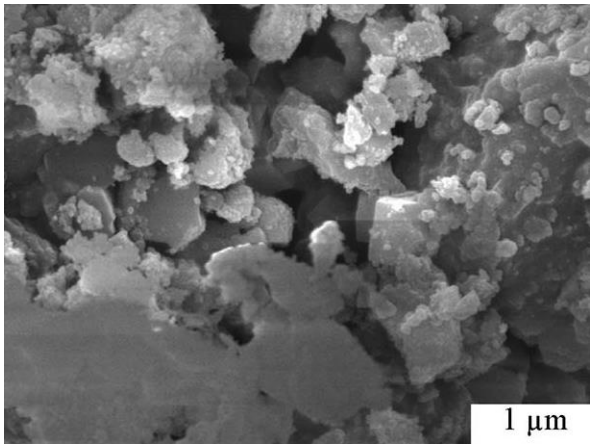


Figure 1. SEM of nano-CeO_2/Al_2O_3

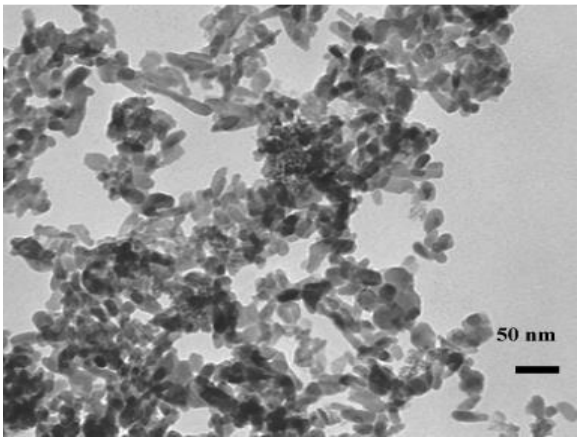


Figure 2. TEM of nano- CeO_2/Al_2O_3

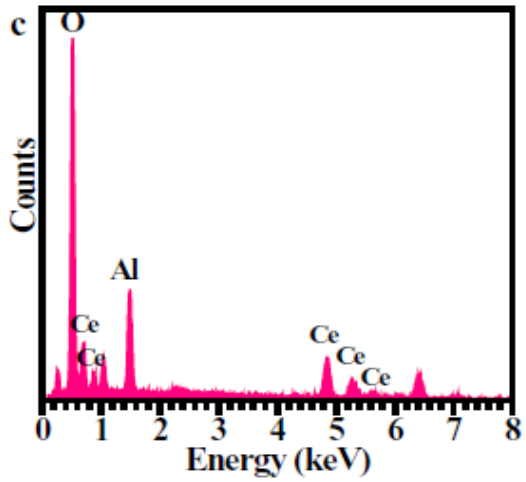


Figure 3. EDAX of nano-CeO_2/Al_2O_3

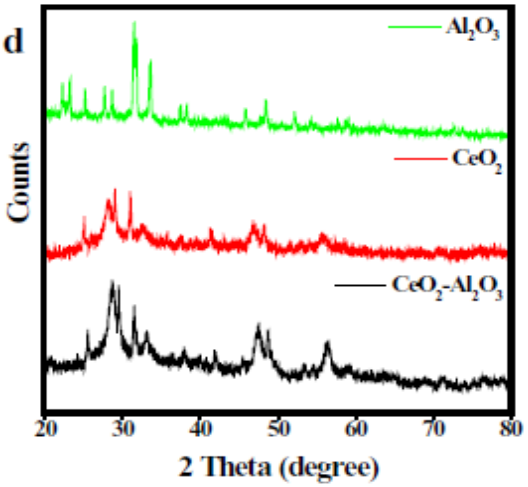
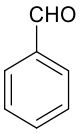
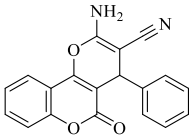
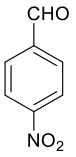
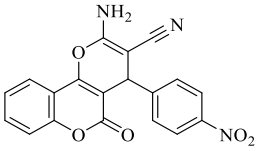
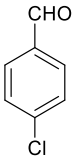
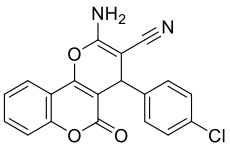
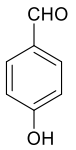
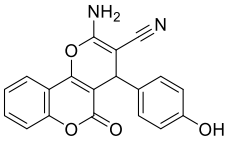
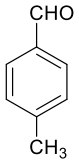
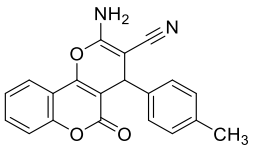


Figure 4. XRD of nano-CeO_2/Al_2O_3

Table 1. Synthesis ofdihydropyrano[c]chromene derivatives

Entry	Aldehyde	Product	Time (min)	Yield (%)	Experimental Melting Point	Theory Melting Point [30]
1		4a 	10	95	255-257	257-256
2		4b 	10	97	261-262	260-257
3		4c 	10	97	265-267	267-266
4		4d 	10	94	268-269	266-262
5		4e 	10	94	266-269	267-265

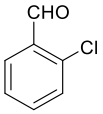
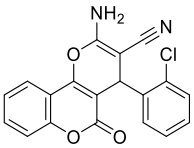
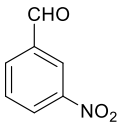
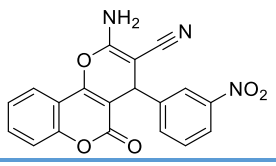
6		4g 	10	96	265-266	266-264
7		4h 	10	97	262-263	263-260

Table 2. Optimization of the amount of nano CeO_2/Al_2O_3 catalyst (g)

Entry	Nano CeO_2/Al_2O_3 (g)	Time (min)	Efficiency (%)
1	0	10	15
2	0.02	10	75
3	0.03	10	80
4	0.05	10	95
5	0.1	10	95

Optimizing reaction time

The model reaction was performed at a different time to obtain the proper time. The results are presented in Table 3. As seen in Table 3, the efficiency increases when the reaction time is increased, and after 10 min it escalates to 95%. After that, it is almost constant. So, the optimal time for performing the reaction was found to be 10 min.

Selection of proper solvent

The model reaction was performed in the presence of different solvents (Table 4). As the Table 4 shows, a high-efficient product is synthesized while using the water. Therefore, water is considered the proper solvent.

The above reaction was compared with the previously performed reactions. As demonstrated in Table 5, the highest efficiency and shortest reaction time is in the presence of nano oxide cerium-aluminum oxide catalyst.

Investigating recyclability of CeO_2/Al_2O_3 catalyst

After the model reaction, 10 mL of ethyl acetate solution was added to the contents on the filter paper, which contains a catalyst. The solution was mixed for 5 min by the magnetic mixer at room temperature. The reaction solution was filtrated and remained on the filter because the catalyst is unsolvable in the ethyl acetate solution. The filter materials were washed several times with acetone to use the catalyst again. After drying up, the reaction was repeated to investigate the catalyst's recyclability. the catalyst could be used up to 5 times and prepare a product with proper efficiency (Table 6).

The proposed mechanism for synthesizing dihydropyrano[c]chromene compounds using nano cerium oxide/aluminum oxide

Aldehyde and malononitrile are condensed at first in the presence of the catalyst, and then they are reacted with 4-hydroxy coumarine, and after the tautomerisism, the desired product is produced (Scheme 2).

Table 3. Comparison of various time for the synthesis of **4a**

Entry	Time(min)	Yield(%)
1	1	40
2	5	75
3	10	95
4	15	95

Table 4. Selecting the suitable solvent

Entry	Solvent	Time(min)	Efficiency(%)
1	CH_3CN	10	88
2	H_2O	10	95
3	CH_2Cl_2	10	70
4	CH_3OH	10	90
5	Solvent-free	10	92
6	C_2H_5OH	10	91

Table 5. Comparison of various catalysts for the synthesis of dihydropyrano[c]chromene derivatives

Entry	Catalyst	Yield (%)	Time(min)	Ref.
1	thiourea dioxide	91	10	[30]
2	DABCO	96	30	[30]
3	pTSA	90	40	[30]
4	TEA	52	120	[30]
5	SiO_2-$NaHSO_3$	48	120	[30]
6	(S)-proline	82	240	[30]
7	Nano-ZnO	81	120	[31]
8	Nano-CuO	90	120	[32]
9	Nano-CeO_2/Al_2O_3	95	10	Present study

Yields refer to isolated products

Table 6. Reuse of the nano CeO_2/Al_2O_3 for synthesis of **4a**

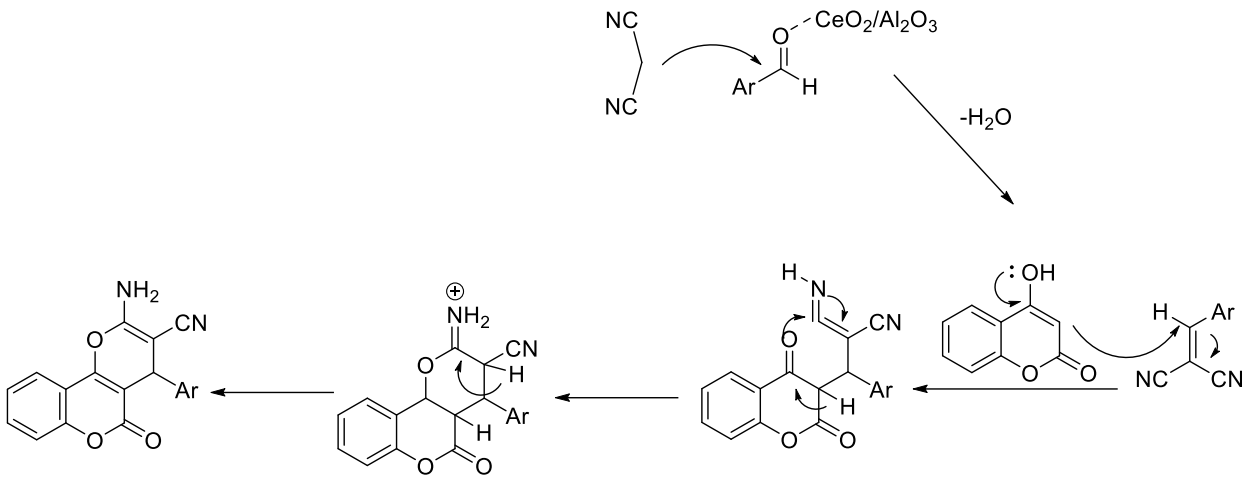
Entry	Run	Yield(%)[a]
1	First	95
2	Second	92
3	Third	90
4	Fourth	88
5	Fifth	85

[a] Isolated yields

Conclusions

In this research study, we developed a novel, simple and efficient method for synthesizing dihydropyrano[c]chromene derivatives by using nano- CeO_2/Al_2O_3 as a catalyst with high efficiency and short time reaction. Nano-CeO_2/Al_2O_3 catalysts are recyclable, heterogeneous, environmentally benign solid catalysts were possessing desirable properties such as high thermal and hydrothermal stability. The target nano CeO_2/Al_2O_3 is a prerequisite in green chemistry. There are some remarkable properties that play prominent roles, such as mildness of the conversion, simple experimental part, ability to be compatible with various functional groups, impressive and efficient yields, short reaction times, and easy

workup procedure. Finally, these features make the target procedure more attractive for synthesizing various derivatives. The results also revealed that, the highest efficiency (95%) in a short time (10 min) was obtained in this study, which is very important compared to other previous methods



Scheme 2. Mechanism of preparation of dihydropyrano[c]chromene

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