

Calcined Dolomite: An Efficient and Recyclable Catalyst for Synthesis of α , β -Unsaturated Carbonyl Compounds

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Abstract

Calcined dolomite was utilized as a low-cost and efficient catalyst for the Knoevenagel condensation of aldehydes with active methylene compounds such as malononitrile and ethyl cyanoacetate to afford substituted α , β -unsaturated carbonyl compounds. Calcination temperature was an important variable which changed the surface areas, textural characteristics and basicity of dolomite catalysts. Among them, natural dolomite was converted to CaO–MgO mixed oxide after calcination at 700 °C, which served as the best catalyst for this reaction. It could be reused for four times without significant decrease of the reactivity. The reaction proceeded smoothly under the magnetic stirring condition at room temperature in excellent yields within short time due to the high surface area and reasonable basicity concentration of dolomite-700 °C catalyst. The attractive features of this procedure were the mild and facile reaction conditions, excellent yields, environmentally friendly reaction profiles and high recyclability, which made it to be an efficient and attractive strategy for the preparation of α , β -unsaturated carbonyl compounds.

Graphical Abstract



Keywords Dolomite · Knoevenagel reaction · Calcination temperature · Basicity · Catalysis

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1 Introduction

Knoevenagel condensation is known as one of the most important carbon–carbon bond formation reactions to manufacture α , β -unsaturated carbonyl compounds [1], which are pivotal intermediates for the production of pharmaceuticals, fine chemicals and polymers etc [2]. This reaction is accomplished by treating a aldehyde with an active methylene compound in the presence of various basic catalysts to afford the desired products [3]. However, there are still a great deal of shortcomings of these catalysts, such as the long reaction time, the

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strict reactive conditions (N_2 atmosphere or high temperature), the special equipments, the contaminated regents, the sophisticated operations, and the highly costly, corrosive and large amounts of catalysts [4]. As a result, a simple, green and recyclable procedure for Knoevenagel condensation with excellent results for all kinds of aldehydes remains a major challenge in organic synthesis.

Dolomite is a mineral material that consists of solid solution of calcium and magnesium carbonates $(CaMg(CO_3)_2)$ with a small amount of mineral impurities [5]. The dolomites in their original form are not suitable as basic catalysts due to its lack of basicity; therefore, the calcination process is neccesary, during which the carbonates in dolomite is decomposed into CaO and MgO thus eliminating CO_2 [6]. Calcined dolomite have served as efficient catalyst in reformation and gasification processes [7, 8], as well as transesterification processes for biodiesel synthesis [9, 10]. CaO and MgO in calcined dolomite exist as stable phases that exhibit an efficient catalytic activity, which is better than that of bulk calcium oxide. However, the study of dolomite as the environmentally benign catalyst for organic synthesis is in demand [11]. Following our research studies on Knoevenagel condensation and catalysis [1, 12, 13], especially for the demand green synthesis [1, 13], calcined dolomite was used as the catalyst for this reaction. In order to obtain a clear interrelationship among the factors of calcined temperature, basicity and components of dolomite catalyst to the activity of Knoevenagel condensation, we investigated their catalytic performances and characterized their structures. The results showed that the reaction proceeded smoothly under mild conditions at room temperature and the products were obtained in excellent yields within short time.

2 Experimental

2.1 Chemicals

The natural dolomite with size smaller than 48 μ m was purchased from Shi Jiazhuang Mineral Powder Factory (Hebei Province, China), whose elemental composition was listed in Table 1. The dolomite powder was calcined in air using a muffle furnace from room temperature to the desired temperature (600, 700, 800 and 900 °C) at a heating rate of 5 °C min⁻¹ and then held at these temperatures for 2 h. All others chemicals with analytical grade were purchased from Shanghai Macklin Biochemical Co., Ltd, China, and used without further treatment.

2.2 Characterizations

The elemental composition of the natural dolomite was analyzed with a PANalytical Axios (MAX) energy dispersive X-ray fluorescence spectrometer (XRF). The thermogravimetric (TG) analysis was conducted on a thermogravimetric analyzer (TGA 2, Mettler, USA) in air flow (200 mL min⁻¹) from room temperature up to 1000 °C (10 °C min⁻¹). N₂ adsorption was performed on a surface area and pore size analyzer (Quantachrome, NOVA 3200e) at -196 °C. The specific surface area was determined according to the Brunauer-Emmett-Teller (BET) method in the relative pressure range of 0.05–0.3. The pore size distribution was calculated with the Barett-Joyner-Halenda (BJH) method using the adsorption isotherm branch. The Fourier-transform infrared spectra (FT-IR) were taken on a Nicolet 380 Fourier Transform-Infrared spectrophotometer (Thermo Electron Corporation, USA) in the range of 400–4000 cm⁻¹. X-ray diffraction (XRD) pattern was obtained by a Rigaku Utima IV (Rigaku Corporation, Osaka, Japan) with a step of 0.02 from 5.0 to 80.0 (wide angle range) using Cu K_{α} radiation ($\lambda = 1.5418$ Å) at 40 kV and 40 mA. The sample was checked with the card number of Joint Committee on Powder Diffraction Standards (JCPDS). Basicity strength (H) of the dolomite catalyst was determined by using Hammett indicator method using bromothymol blue (H_=7.2), phenolphthalein (H_=9.8), dinitroaniline (H = 15.0) and nitroaniline (H = 18.4) as Hammett indicators [5, 6]. Total basicity number of the dolomite catalyst was determined by volumetric titration using Hammett indicator-benzoic acid standard solution. The morphology of the samples was visualized using an emission scanning electron microscope (SEM) (FEI Nova NanoSEM 450) and transmission electron microscopy (TEM) (JEM-2010F, JEOL) equipped with an energy-dispersive X-ray spectroscopy (EDX) detector. Melting points (M.p.) were determined by using XT-4 micromelting point apparatus (Beijing Taike Instrument Company, China). ¹H NMR spectra were taken on an EFT-60 NMR spectrometer (Anasazi Instruments, USA) using CDCl₃ as solvent and TMS as the internal standard.

2.3 General Procedure for Knoevenagel Condensation

Typically, benzaldehyde (20 mmol) and the active methylene compound (20 mmol) were mixed thoroughly in a solvent, and then the appropriate amount of dolomite catalyst was added. The reaction mixture was stirred for the specified time at room

Table 1Elemental compositionof the natural dolomitedetermined by XRF analysis

Components	CaO	MgO	SiO_2	Fe ₂ O ₃	Al_2O_3	Cl	Others
Contents (wt%)	66.35	32.73	0.40	0.25	0.18	0.03	0.06

temperature. After completion of the reaction, the reaction mixture was then collected and dissolved in hot ethanol, and the catalyst was removed by filtration. The filtrates were then cooled to afford pure crystals. The recovered catalyst could then be washed sequentially with anhydrous ethanol, dried and recalcined at 700 °C for reuse in the next reaction cycle. All the products were previously reported and were characterized by comparing with those M.p., IR and ¹H NMR.

3 Results and Discussion

3.1 Catalyst Characterizations

3.1.1 XRF

The elemental composition of the natural dolomite was determined according to the qualitative and quantitative characterization by X-ray fluorescence assessment (XRF) and the result of XRF analysis was given in Table 1. As seen, the purity of the natural dolomite was higher than 99% with small amounts of impurities including SiO₂, Al₂O₃ and Fe₂O₃ etc.

3.1.2 TGA

Figure 1 shows the result of TG analysis of natural dolomite. A broad decomposition peak (558–786 °C) with the maximum at 725 °C was observed for the dolomite, and the residual mass attained 64% at around 800 °C during the TGA experiment. As reported in the literatures [8, 9], the devolatilization of CaMg(CO₃)₂ was determined by the pressure of CO₂. The calcination of dolomite took place in a two-steps-process at high partial pressure of CO₂, in which



Fig. 1 Thermogravimetric analysis of natural dolomite in air flow of 200 mL min⁻¹ at the heating rate of 10 $^{\circ}$ C min⁻¹

CaMg(CO₃)₂ was first decomposed to MgO and CaCO₃ in the temperature range of 780–800 °C, and then the decomposition of CaCO₃ to CaO carried out at 880–900 °C. On the other hand, the calcination of dolomite occurred in one step to MgO and CaO at around 700 °C with low partial pressure of CO₂ (< 200 Torr). Apparently, the devolatilization of CaMg(CO₃)₂ in this work was a two-steps-process in the wide temperature range of 558–786 °C, and CO₂ together with other volatile impurities over the dolomite leaded to the weight loss during calcination. The experimental value in this work correlated with the theoretical and reported values in the literature [8].

3.1.3 Nitrogen Adsorption

Figure 2 shows the N_2 adsorption-desorption isotherms and pore size distribution (PSD) curves of the natural and calcined dolomite catalysts. For the natural dolomite, there were negligible pores with the almost coincident adsorption and desorption isotherm profiles. On the contrary, the adsorption-desorption isotherm profiles of all the calcined samples were all compliance with the type IV isotherms, which contained hysteresis loops typical to the type H2 [14, 15]. The hysteresis loop of the samples located at P/ $P_0 = 0.85 - 1.0$, indicating the pores in the calcined samples were from the aggradation of nanoparticles [16]. Apparently, the calcination process facilitates cracking of dolomite surface due to the devolatilization of CO₂ from the internal of dolomite. Furthermore, the higher nitrogen uptake of calcined dolomite at $P/P_0 = 1.0$ can indicate the presence of an extensive network of pores. Moreover, the PSD curves of all the samples were similar except for dolomite-700 °C, which obtained extensive mesporous structure at the reasonable calcination temperature. However, the excessive high temperatures had adverse effect on the high-surface-area of the calcined dolomite. Table 1 showed the surface and textural properties of natural and calcined dolomite. Natural dolomite exhibited lowest surface area; while after calcination, the calcined dolomite showed larger pore volume and higher surface area compared with those of natural dolomite. Among them, dolomite-700 °C exhibited the highest surface area and the largest pore volume. This was because the mesporous pores were formed through the decomposion of dolomite during the calcination and the collapse of pores occurred at the higher temperatures.

3.1.4 FT-IR

Figure 3 presented the FT-IR spectra of natural and calcined dolomite. The spectrum of natural dolomite showed two peaks at 731 and 879 cm⁻¹. The former peak at 731 cm⁻¹ was respected to the non-fundamental combination frequency and in plane bending mode of CO_3^{2-} part

Fig. 2 N₂ adsorption isotherms (a) and pore size distribution curves (b) of the natural and calcined dolomite (for clarity, the isotherm of natural dolomite, dolomite-600 °C, dolomite-700 °C, dolomite-800 °C and dolomite-900 °C was vertically shifted for 160, 140, 60, 40 and 15 cm³ g⁻¹, respectively)



175

150

125

100

75

(a)

600°C

natural dolomite

Fig. 3 FT-IR spectra of natural and calcined dolomite

of dolomite [5, 10]. The latter peak at 879 cm⁻¹ was significant to the carbonate bending mode [5, 10]. All the peaks associated with CO₃²⁻ disappeared after calcination above 800 °C, indicating that dolomite decomposed to oxides of calcium and magnesium. Also, the FT-IR spectra of CaO and MgO were shown in Fig. 3. Apparently, the CaO and MgO combinations showed different IR spectra compared with that of CaO and MgO. In addition, a little amount of adsorbed surface water was evidenced by the presence of the broad OH stretching of hydrated carbonate at 2500–3500 cm⁻¹ [17].



Fig. 4 XRD patterns of natural and calcined dolomite

3.1.5 XRD

Figure 4 showed the XRD patterns of the natural and calcined dolomite. For the natural dolomite, the diffraction peaks at 30.8, 41.1, 45.0, 50.5, 51.0 and 64.5° which were characteristic peaks of CaMg(CO₃)₂ (JCPDS 01-073-2361) [5]. After calcination at 600 °C, there was no obvious change on its XRD patterns compared with that of natural dolomite. Apparently, there would be no significant decomposition of dolomite at 600 °C. For the XRD patterns of dolomites calcined at higher temperatures, the new peaks were detected at 32.0, 37.2, 53.7 and 64.1° corresponding to the calcium oxide (JCPDS 01-077-2010) generated by (110), (200), (220) and (311) reflections, respectively. Meanwhile, the peaks at 37.4 and 62.16° corresponded by (111) and (220) reflections were the characteristic peaks of magnesium oxide

(JCPDS 01-087-0651). In addition, the crystallinity of CaO and MgO at 800 and 900 $^{\circ}$ C was much stronger than that of dolomite-700 $^{\circ}$ C, indicating that the further crystallization occurred at high temperatures [18]. It was worth noting that the diffraction peaks of calcined dolomite had no peaks that corresponded to those of the natural dolomite, which provided the further evidence of the conversion of natural dolomite.

3.1.6 SEM and TEM Observations

Figure 5 exhibited the SEM images of the natural and 700 °C-calcined dolomite. The rough surface over calcined dolomite could be observed, which was formed by cracking the natural dolomite surface by CO_2 decomposion during calcination process [19]. However, the morphologies of both natural and calcined dolomite observed by TEM was similar because their surface area were both relatively low with 1.36 and 20.86 m² g⁻¹, respectively (Fig. 6a–d). In addition, the energy-dispersive X-ray spectroscopy (EDX) measurement of the dolomite-700 °C was also conducted and its profile was shown in Fig. 6e. The exclusive peaks for Ca, Mg, and O were clearly observed; also, the weak peaks attributed to the imprities such as Si and Fe elements, which was coincident with the results of XRF analysis.

3.1.7 Hammett Indicator Method

Basicity strength, total basicity number and basicity concentration of the natural and calcined dolomite are listed in Table 3. As seen, the effect of calcination temperature on basicity of natural dolomite and calcined dolomites was significant. Natural dolomite and dolomite-600 °C exhibited basicity strength of H_<7.2, indicating that the dolomite was not decomposed at low tempertaure. Above 700 °C, the calcined dolomite had higher basicity strength of 15 < H_<18.4. Meanwhile, the total basicity number was positively related with the calcination temperature [6, 10, 16]. Compared with dolomite-700 °C, the value of dolomite-800 °C increased rapidly, while no further increment was found on dolomite-900 °C. On the contrary, the change regulation was more complicated due to the difference of their surface areas, and dolomite-800 °C had the maximum value among all the samples [20].

3.2 Calcined Dolomite-Catalyzed Knoevenagel Reaction

3.2.1 Effect of Calcination Temperature

Table 4 presented the effect of calcination temperature of dolomite on Knoevenagel condensation reaction of benzaldehyde with malononitrile. For natural dolomite, the yield was only 4% after 480 min (Table 4, entry 1), indicating its poor catalytic activity for Knoevenagel reaction. This was because it was consisted of CaMg(CO₃)₂ with low H_ value and total basicity number. After calcination, the catalytic activity could increase obviously. Among them, dolomite-700 °C showed the highest activity with 96% yield in 45 min (Table 4, entry 3). However, the higher temperature had the adverse effect on this reaction with longer reaction time (Table 4, entries 4 and 5). As mentioned above, the results of nitrogen adsorption, XRD patterns, FT-IR spectra and basicity strength presented evidence that the changes of composition, textural structure and basicity of dolomite occurred during calcination process. At 600 °C, the decomposition reaction of $CaMg(CO_3)_2$ was incomplete with very low H_ value (<7.2), which resulted in its low activity. After calcination at high temperatures (700, 800 and 900 °C), the complete decomposition of dolomite performed and the main components of the samples were CaO and MgO (Fig. 4). Thus, their H_ values increased obviously in the range of 15-18.4. In addition, the decomposition of dolomite leaded to the high specific surface areas especially at the relatively low temperature of 700 °C (Table 2). Meanwhile, the total basicity number increased with the increase of calcination temperature (Table 3). However, the basicity concentration showed complicated change rule, and dolomite-700 °C showed the lowest value among the calcined dolomite (Table 3). As we know, Knoevenagel condensation reaction is a typical weak-base-catalyzed reaction, and the higher basicity can lead to severe side reactions and low









yield [4, 12]. This might be the reason for high activity of dolomite-700 °C catalyst. In this work, dolomite-700 °C showed the low basicity concentration and total basicity number as well as the high enough basicity strength, which resulted in its highest catalytic activity for Knoevenagel reaction. In short, combined with the results of Tables 3 and 4, it could be seen that the basicity strength, total basicity

number and basicity concentration of the dolomite catalysts were crucial for Knoevenagel reaction.

3.2.2 Effect of Solvent

Developing green chemical methods is one of the most important purposes of organic synthesis at present. One of the

 Table 2
 Textural properties of the natural and calcined dolomite

Sample	$S_{\rm BET} ({\rm m}^2 {\rm g}^{-1})^{\rm a}$	$V_{\rm p} ({\rm cm}^3{\rm g}^{-1})^{\rm b}$	$D_{\rm p} ({\rm nm})^{\rm c}$
Natural dolomite	1.36	0.01	29.4
Dolomite-600 °C	2.45	0.01	16.3
Dolomite-700 °C	20.86	0.10	19.1
Dolomite-800 °C	5.07	0.03	23.7
Dolomite-900 °C	5.83	0.03	20.6

^aS_{BET}, surface area of the sample derived from BET equation

 $^{\rm b}V_{\rm P}$ pore volume of the sample obtained from the volume of nitrogen adsorbed at the relative pressure of 0.99

^c $D_{\rm P}$, average pore diameter of the sample derived from BJH method using the following equation $D_{\rm P} = 4 \times \frac{V_{\rm P}}{S_{\rm ner}}$

 Table 3
 Basicity strength, total basicity number and basicity concentration of the natural and calcined dolomite

Sample	Basicity strength (H_) ^a	Total basic- ity number (mmol g ⁻¹) ^a	Basicity concentra- tion (µmol m ⁻²) ^b	
Natural dolomite	<7.2	0.04	29.41	
Dolomite-600 °C	<7.2	0.67	273.47	
Dolomite-700 °C	15 < H_<18.4	3.50	167.79	
Dolomite-800 °C	15 < H_<18.4	11.00	2169.63	
Dolomite-900 °C	15 < H_<18.4	11.44	1962.26	

^aMeasured by the Hammett indicators method

^bBasicity concentration=total basicity number/specific surface area

 Table 4
 Effect of calcination temperature of dolomite on Knoevenagel condensation of benzaldehyde with malononitrile



Entry	Catalyst	Time (min)	Yield (%) ^a
1	Natural dolomite	480	4
2	Dolomite-600 °C	200	85
3	Dolomite-700 °C	45	96
4	Dolomite-800 °C	85	99
5	Dolomite-900 °C	117	93

Reaction conditions: benzaldehyde (20 mmol), malononitrile (20 mmol), catalyst (0.1 g), solvent-free, magnetic stirring, room temperature

^aIsolated yield

fundamental challenges and ultimate goals for organic reactions is to perform the reaction under solvent-free condition or in environmentally friendly solvents [21]. Here, in order

 Table 5
 Effect of solvent on Knoevenagel condensation of benzaldehyde with malononitrile



Entry	Solvent	Time (min)	Yield (%) ^a	
1	Solvent-free	45	96	
2	CH ₃ OH	6	93	
3	C ₂ H ₅ OH	6	92	
4	<i>n</i> -C ₃ H ₇ OH	13	91	
5	<i>n</i> -C ₄ H ₉ OH	18	92	
6	H ₂ O	2.5	90	
7	$C_2H_5OH-H_2O(3:1)^b$	2	86	
8	C ₂ H ₅ OH–H ₂ O (1:1) ^b	1.5	89	
9	C ₂ H ₅ OH–H ₂ O (1:3) ^b	2	85	

Reaction conditions: benzaldehyde (20 mmol), malononitrile (20 mmol), dolomite-700 °C (0.1 g), solvent (4 mL), magnetic stirring, room temperature

^aIsolated yield

^bVolume ratio

to investigate the influence of the solvents [22], the model reaction of benzaldehyde with malononitrile was carried out through magnetic stirring method in various solvents and also under solvent-free condition at room temperature. As shown in Table 5, the reaction under solvent-free condition finished in 45 min with the yield of 96% (Table 5, entry 1). However, the reaction proceeded more rapaidly in solvents such as lower aliphatic alcohols and H₂O with similar yields (Table 5, entries 2-6). Among them, H₂O was the best solvent for this reaction. As we know, the order of polarity is $H_2O > CH_2OH > C_2H_5OH > n - C_3H_7OH > n - C_4H_0OH$ [23]. Apparently, the higher polarity of solvent is propitious to increase the catalytic activity in this work. Meanwhile, the reaction could be further improved using the mixed solvents of enthanol and H₂O. The mixed solvent of ethanol and H₂O seemed to be much more efficient for this reaction (Table 5, entries 7-9), indicating that the different volume ratio had obvious effect on reaction activity. Among them, this reaction finished in the shortest time (1.5 min) with the yield of 89% in a mixture of ethanol and H₂O (1:1, volume ratio). We know that the aromatic aldehydes and the active methylene compounds are all hydrophobic, which resulted in the poor interrelationship between the substrates and catalyst in the presence of water. However, all the substrates have high solubility in ethanol. Thus, the mixed solvent of water and ethanol could not only increase the solubility of the substrates, but also provide the reaction environment with high polarity, which

leaded to the high activity in the mixed solvent. From both environmental and economic points of view, using aqueous media to perform organic reactions had attracted considerable interest because water was considered to be the most environmentally acceptable, safe and inexpensive solvent [24]. As we all knew that ethanol was an environment-friendly solvent, therefore, the reactions used ethanol and water as solvent in this work. This operation allowed Knoevenagel condensation

 Table 6
 Effect of catalyst amount on Knoevenagel condensation of benzaldehyde with malononitrile



Entry	Amount of catalyst (g)	Time (min)	Yield (%) ^a	
1	0.1	1.5	89	
2	0.3	1.0	93	
3	0.5	46 s	97	
4	0.75	45 s	89	

Reaction conditions: benzaldehyde (20 mmol), malononitrile (20 mmol), dolomite-700 °C, magnetic stirring, ethanol and H_2O (each 2 mL), room temperature ^aIsolated yield

to be performed in a very simple, cheap and green manner. Based on the above results, the remaining of reactions were carried out in the mixture of ethanol and $H_2O(1:1)$.

3.2.3 Effect of Amount of Catalyst

Continuing with the above work, in order to evaluate effect of amount of catalyst on Knoevenagel condensation, we investigated its efficiency over the model reaction between benzaldehyde and malononitrile through conventional magnetic stirring method in the mixture of ethanol and H_2O (1:1) solvent. As seen in Table 6, the reactions could carry out in short reaction times with high yields. The yield was 89% in 1.5 min, when the amount of dolomite-700 °C was 0.1 g (Table 6, entry 1). After the increase of amount of dolomite-700 °C, the reaction time was significantly reduced and the yield increased obviously. When the amount of dolomite-700 °C catalyst was 0.5 g, the reaction time was only 46 s with the yield of 97% (Table 6, entry 3). There was no obvious increase in catalytic activity while excess catalyst was used. Thus, the remaining reactions were carried out in the presence of 0.5 g dolomite-700 °C.

3.2.4 Universality of Dolomite Catalyst for Knoevenagel Condensation

After optimising the reaction conditions, various aromatic aldehydes were treated with the active methylene compounds

Table 7	Knoevenagel	condensation	catalyzed	by (dolomite	through	magnetic	stirring meth	lod
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RCHO +
$$H_2C_X \xrightarrow{CN} \frac{\text{Dolomite-700°C, 0.5 g}}{\text{EtOH and } H_2O} \xrightarrow{R} C = C_X$$

Entry	R	Х	Time (min)	Yield (%) ^a	M.p. (°C)	
					Found	Reported
1	C ₆ H ₅	CN	46 s	97	82-83	82-83 [24]
2	$2-ClC_6H_4$	CN	1	97	94-95	95-96 [25]
3	4-ClC ₆ H ₄	CN	22 s	85	160-162	160–162 [<mark>26</mark>]
4	2, 4-Cl ₂ C ₆ H ₃	CN	2	96	153-155	154–155 [27]
5	4-CH ₃ OC ₆ H ₄	CN	29 s	100	110-112	110–112 [24]
6	4-CH ₃ C ₆ H ₄	CN	45 s	89	131-134	132–134 [26]
7	4-OHC ₆ H ₄	CN	4	96	184-185	183–184 [<mark>28</mark>]
8	Vanillin	CN	5	90	135-137	135–136 [<mark>25</mark>]
9	2-Furyl	CN	1.5	93	64-66	65–66 [24]
10	C ₆ H ₅	COOEt	85	96	47–49	48–49 [29]
11	4-ClC ₆ H ₄	COOEt	4.5	99	86-88	86-88 [26]
12	$4-CH_3C_6H_4$	COOEt	5	99	92-93	92–93 [30]

Reaction conditions: benzaldehyde (20 mmol), the active methylene compound (20 mmol) and dolomite-700 $^{\circ}$ C (0.5 g) in a mixture of ethanol and H₂O (1:1) at room temperature

^aIsolated yield

 Table 8
 The reuse of dolomite for Knoevenagel condensation of benzaldehyde and malononitrile

Cycle	1	2	3	4	5
Time (s)	46	55	45	58	65
Yield (%) ^b	97	100	97	89	97

Reaction conditions: benzaldehyde (20 mmol), malononitrile (20 mmol), dolomite-700 °C, magnetic stirring, ethanol and H_2O (each 2 mL), room temperature

^aIsolated yield

in the presence of dolomite-700 °C catalyst using the conventional magnetic stirring method in a mixture of ethanol and H₂O (1:1) at room temperature. Overall, it afforded the desired α , β -unsaturated carbonyl compounds as the single products, and all of the comparative results are shown in Table 7.

The aldehydes, containing electron-withdrawing group (chloro), and electron-donating groups such as methoxy, methyl, hydroxyl etc, all gave the desired products in excellent yields in short time. In addition, furfural could also react rapidly with malononitrile (Table 7, entry 9). We found that the reaction proceeded much fast with more acidic malononitrile (Table 7, entries 1-9) than with ethyl cyanoacetate (Table 7, entries 10-12). For the reactions with malononitrile, the reactions took place in dozens of seconds or several minutes, while the reactions of ethyl cyanoacetate with the same aromatic aldehydes needed longer time. This was because the electron-withdrawing ability of the CN group is stronger than that of the carbonyl or carboxylic group, the methylene group of malononitrile is more activated than ethyl cyanoacetate, and readily reacts with aromatic aldehydes [25]. In addition, when ethyl cyanoacetate was used as the active methylene compound, only E isomers were obtained because of steric effects [26].

3.2.5 Catalyst Reusability Test

The reusability experiments were performed to investigate the stability of dolomite catalyst under the optimized reaction conditions using benzaldehyde and malonitrile as model substrates. After thermal filtration in ethanol solution and recalcination at 700 °C, the dolomite-700 °C catalyst could be reused for four times (total five cycles) without significant decrease of the reactivity (Table 8), indicating the high reusability of dolomite catalyst in this work. Furthermore, all the recovered ctalysts were characterized by XRD and FT-IR. As seen in Fig. 7, the textural properties and functional groups of the dolomite-700 °C catalysts remained unchanged after each cycle, indicating that the recovery procedure of dolomite catalyst in this work was reasonable and efficient.

4 Conclusions

In summary, we have demonstrated a facile and efficient method for the Knoevenagel condensation of aromatic aldehydes with the active methylene compound in the presence of dolomite catalyst. The reactions were carried out smoothly under mild conditions at room temperature. The reaction could be significantly improved in the mixed solvent of ethanol and water with volume ratio of 1:1. Calcination temperature changed the surface area, textural characteristics and basicity of dolomite, and dolomite-700 °C showed the highest activity due to its high surface area and reasonable basicity concentration. It could be reused for four times without significant decrease of the reactivity. The attractive features of this procedure were the mild reaction conditions, high yields, environmentally friendly reaction profiles, recyclable and operational simplicity. All of which make it a useful and attractive strategy for the preparation of α , β -unsaturated carbonyl compounds.





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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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