

# High Efficient Aldol Condensation Reaction Utilizing Modified Calcium Oxide as Stable Solid Base Catalyst<sup>1</sup>

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**Abstract**—Aldol condensation of acetophenone and benzaldehyde, as well as various benzaldehydes was carried out efficiently to produce chalcone with a good selectivity and high yields by using modified CaO as a solid base catalyst. Stability and catalytic activity of commercial CaO were significantly improved after modifying calcium oxide with bromobenzene in a simple way. An Aldol yield higher than 98.9% was obtained after the reaction was conducted for 3 h. This time interval is considerably shorter when compared to a period of 12 h needed for the commercial CaO to reach 92.1% yield under optimum activation. The high catalytic activity of modified CaO suggests that heterogeneous aldolisation was greatly improved by changing its hydrophilic properties. The influence of several reaction parameters, such as temperature and catalyst loading, was investigated. The humidity test over modified CaO reveals that the basic sites of modified CaO are resistant to CO<sub>2</sub> and moisture. The type of aldehyde has great influence on the yield of Aldol condensation. Based on the results of characterization by Fourier transform-infrared spectrometry (FT-IR) and thermogravimetric measurements (TG), it was concluded that the modifier was chemically bonded to the surface of CaO and nearly no Ca(OH)<sub>2</sub> was formed during the modification process.

**Keywords:** Aldol condensation, CaO, surface modification

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The Aldol condensation involving C-C bond formation has numerous applications in the synthesis of fine chemicals. This kind of reaction can proceed catalytically in the presence of a strong base or acid in liquid phase [1–3]. For the aim of environmental protection it is desirable to find solid bases which could substitute liquid catalysts and would also preserve all the advantages of heterogeneous catalysis, i.e. ease of separation of the products, insignificant corrosion of the reactor, and possible regeneration of the catalyst. Different families of solid bases were found to be active catalysts in this reaction, including alkali-exchanged zeolites [4], ion-exchange resins [5, 6], alumina-supported hydroxide [7, 8], Mg–Al hydrotalcite and alkaline-earth metal oxides [9]. Because of its strong basicity hydrotalcite was regarded as the most suitable candidate for industrial application. The published method for Mg–Al hydrotalcite activation included a liquid-phase reconstruction to create surface sites with a narrow base-strength distribution [10]. It is worth noting that at high conversions reached with these solids the yields are generally modest. Furthermore, the basic sites on the surfaces of alkaline-earth metal oxides or hydrotalcite-like samples are easily poisoned

by air due to adsorption of CO<sub>2</sub> and H<sub>2</sub>O [11]. Calcium oxide, an alkaline-earth metal oxide with strong basicity and low cost, is widely used in various base-catalyzed reactions. However, the industrial application of this solid base is limited since it is not stable upon exposure to moist air. It was repeatedly reported that all operations during preparation, processing, storage and use of the catalyst were conducted extremely carefully in an inert gas atmosphere to avoid contact with air. Nevertheless, independently of the catalyst nature a single contact between reagents and catalysts cannot be ruled out and that contact can cause loss of the catalytic activity to a level below that of homogeneous strong base, such as sodium hydroxide. Herein, the aim of this study was to develop an active CaO with a high efficiency for the Aldol condensation of acetophenone and various benzaldehydes and good stability in moist air. The modifying conditions and various reaction conditions were also investigated.

## EXPERIMENTAL

### *Modification of CaO [12, 13]*

A simple method was used for the surface modification of CaO. An aliquot (2.8 g) of the 0.15–0.095 mm

<sup>1</sup> The article is published in the original.

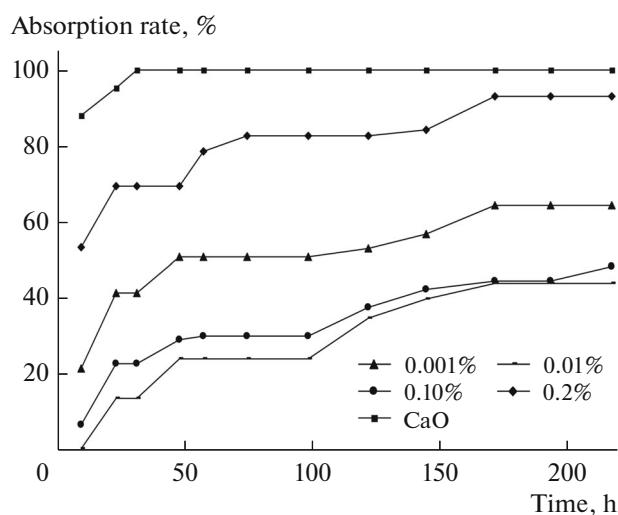


Fig. 1. Moisture absorbing rate over commercial CaO and modified CaO with various benzyl bromides.

fraction of commercial CaO (China National Medicines Co., Ltd.) was added into the bromobenzene (Sigma-Aldrich, AR)/methanol solution (40 mL) under stirring at room temperature. The content of bromobenzene was varied from 0.01 to 0.5%. The mixture was stirred for 24 h, the solid was then filtered and washed with methanol to remove excess modifier. Vacuum drying yielded the modified CaO catalyst.

#### Humidity Test

Fractions of commercial CaO and modified CaO catalyst were transferred into the container and stored at room temperature over saturated water vapour for several days to maintain the adsorption equilibrium with water. The samples were weighed at regular time intervals. The extent of moisture adsorption (%) was evaluated using the following equation:

$$w\% = \frac{56\Delta m}{18m_0} \times 100\%,$$

where  $\Delta m$  denotes an increase in the weight of the solid, and  $m_0$  is the initial weight of the solid.

#### Activity Test

In a typical procedure, 0.6 mmol of acetophenone (99%) and 0.5 mmol of purified benzaldehyde (99.9%) (mole ratio of benzaldehyde: acetophenone = 1.2 : 1) were added into 20 mL MeOH in a 50-mL round bottom flask equipped with magnetic stirrer and condenser. The mixture was stirred for 15 min and then about 0.25 mmol of catalyst was introduced at a constant temperature. The reaction mixture was heated at a desired reaction temperature (20–65°C) at atmospheric pressure. When the reaction was completed the mixture was cooled, the solution was sepa-

rated from the solid and analyzed by gas chromatography using a flame ionization detector, HP-5 capillary column (30 m long, i.d. 0.25 m) programmed from initial temperature of 50 to final temperature of 280°C with N<sub>2</sub> (1.5 mL/min) as a carrier gas. The yield was calculated by area normalization method on a carbon basis and the carbon balances data were good at around 100 ± 5%.

#### Catalysts Characterization

The Fourier transform-infrared (FT-IR) spectrophotometer Nicolet Nexus 670 (Nicolet, United States) was used to identify the surface group of the catalyst. Thermogravimetric (TG) experiments were carried out using Q600 SDT thermal analysis machine (TA Instruments, United States) under a flow of air at temperatures ranging from 25 to 800°C with a ramping rate of 10 deg/min.

## RESULTS AND DISCUSSION

#### Humidity Test

Since CaO can sorb considerable amounts of water, the poisoning effect of H<sub>2</sub>O adsorption during catalyst preparation is the most important issue. In order to improve stability of CaO in air, the surface of CaO was modified by different amounts of bromobenzene used as a hydrophobic reagent. The effect of modifier loading on the stability of modified CaO in air was also investigated. Humidity tests were carried out with the samples of CaO modified by different amounts of benzyl bromide (from 0.001 to 0.2 wt %). The extent of moisture adsorption for these samples as a function of time is illustrated in Fig. 1. It can be readily seen that the degree of moisture absorption calculated from the incremental weight increase of CaO continues to rise with time for all samples. However, obvious differences in the patterns of behaviour of commercial CaO and calcium oxide modified by benzyl bromide can be traced. For the unmodified CaO material, the extent of moisture absorption increases rapidly and reaches a nearly 100% level within 50 h, while very low weight increment can be found over modified CaO at the same time. The sample of CaO modified with 0.1% bromobenzene shows the slightest moisture resistance. It can be concluded that the surface modification greatly improves the moisture resistance of commercial CaO and this improvement can be explained by the formation of hydrophobic layer over catalyst surface caused first of all by the introduction of the aromatic group of bromobenzene. A further increase in the modifier loading deteriorates the resistance to moisture of the modified CaO because the reaction between bromobenzene and hydroxyl over surface of CaO results in the increased formation of CaBr<sub>2</sub> species, which have high affinity to water.

Figure 2 shows the FT-IR spectra of commercial CaO and modified CaO. The spectra display bands at

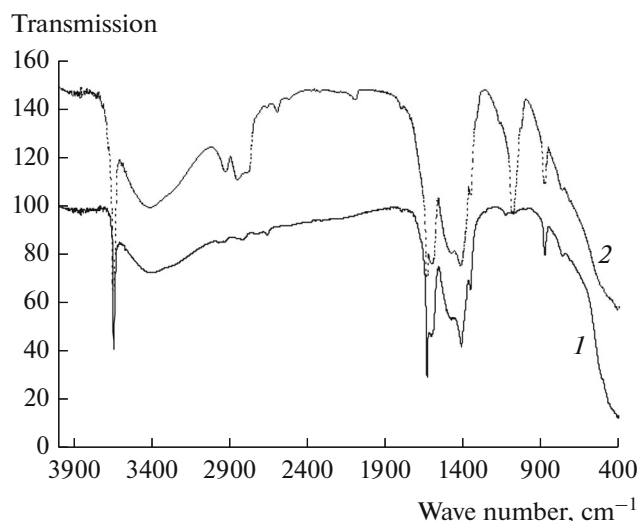


Fig. 2. IR pattern of commercial CaO (1) and modified CaO (2).

867 and  $1477\text{ cm}^{-1}$  corresponding to vibration modes of mono- and bidentate carbonates. The presence of carbonates is also evident from the characteristic absorption of C=O between  $2000$  and  $1600\text{ cm}^{-1}$  that indicates the presence of calcium carbonate formed in both catalysts. However, a minor difference in the intensity of bands suggests that carbonate formation over modified CaO involving  $\text{CO}_2$  from air is negligible. The bands at  $1621$  and  $3460\text{ cm}^{-1}$  are associated with adsorbed water. The important features of the modified CaO appear in the C–H (alkane) stretching ( $2800$ – $3000\text{ cm}^{-1}$ ) and bending ( $1440\text{ cm}^{-1}$ ) vibrations [14]. Vibrations of aromatic carbon double bond cause the increase in the intensity of bands at  $1600$  and  $1580\text{ cm}^{-1}$  where as stretching vibrations of the aromatic carbon-hydrogen ( $3060\text{ cm}^{-1}$ ) provide evidence of the formation of phenyl groups [15]. Another difference between the spectral pictures of modified CaO and commercial CaO is the vibration around  $1080\text{ cm}^{-1}$ , which is assigned to the stretching vibration of –C–O as a result of the reaction between modifier and hydroxyls on the surface of CaO. All these observations suggest that modification of commercial CaO was successful.

Figure 3 shows the results of TG/DSC thermogravimetric analysis of commercial CaO and modified CaO. The samples are characterized by TG curves that exhibit two steps between  $400$  and  $800^\circ\text{C}$  due to the loss of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . Furthermore, the DTG curve of the modified CaO shows two broad peaks at  $450$  and  $700^\circ\text{C}$  corresponding to the decomposition of  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$  formed by the hydration and carbonation of CaO in the course of storage and preparation. Both peaks are shifted to higher temperatures compared with those exhibited by commercial CaO ( $339$  and  $614^\circ\text{C}$ ). It can be therefore inferred that

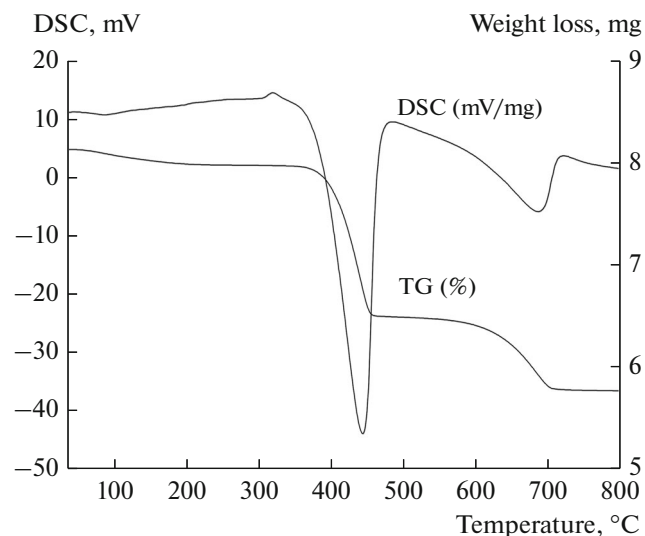


Fig. 3. TG/DSC thermogram of modified CaO.

by modifying CaO it is possible to improve thermal stability of calcium oxide.

#### Catalytic Activity

Homogeneous basic catalysts are efficient for catalysing Aldol condensation with good yield and selectivity. Different basic catalysts were investigated in our work with results of condensation of acetophenone and benzaldehyde shown in Fig. 4. The reaction was conducted at room temperature for 6 h, the amount of catalyst in all runs was 20 wt %. It can be easily recognised that in the presence of the homogeneous catalysts the yields increased with increasing catalyst

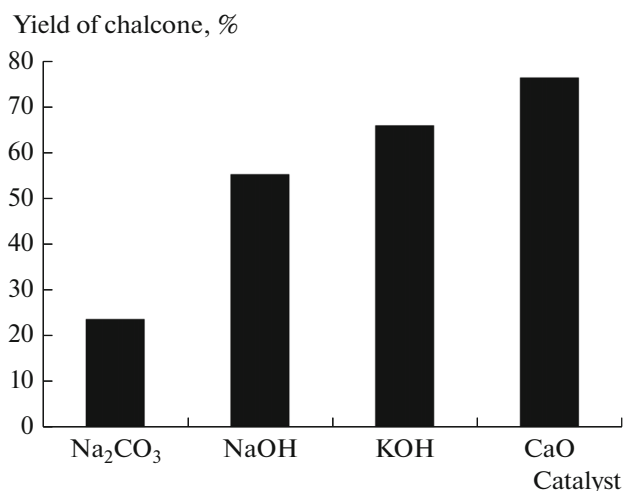


Fig. 4. The catalytic performances of various catalysts in Aldol reaction of bromobenzene and benzaldehyde. Catalyst amount—20%, reaction time—12 h, bromobenzene/benzaldehyde = 1.2 : 1, reaction temperature— $60^\circ\text{C}$ .

**Table 1.** Effect of the catalyst amount on the yield of chalcone in condensation of acetophenone using commercial CaO as a catalyst

Catalyst, wt %	Yield of chalcone, %
5	62.4
10	68.5
20	75.8
40	71.4
60	67.1

Reaction conditions: 5.0 mmol acetophenone, 7.5 mmol purified benzaldehyde/methanol (20 mL), ambient temperature, 6 h.

**Table 2.** Effect of reaction temperature on the yield of chalcone in the condensation of acetophenone in the presence of commercial CaO catalyst

Temperature, °C	Yield of chalcone, %
30	76.1
40	78.4
50	80.1
60	82.3
65	82.6

Reaction conditions: 5.0 mmol acetophenone, 7.5 mmol benzaldehyde/methanol (20 mL), 20% of the catalyst, 6 h.

**Table 3.** Effect of acetophenone/benzaldehyde mole ratio on yield of chalcone in the condensation of acetophenone using commercial CaO as a catalyst

Acetophenone/benzaldehyde ratio	Yield of chalcone, %
1 : 1.1	78.8
1 : 1.2	82.3
1 : 1.3	83.5
1 : 1.5	85.8
1 : 1.8	81.9
1 : 2.0	78.9

Reaction conditions: 20% of the catalyst, 60°C, 6 h.

basicity and the most efficient catalyst was KOH. Low catalytic activity observed in the presence of Na<sub>2</sub>CO<sub>3</sub> is due to its weak basicity. Contrary to the expectation, CaO, a heterogeneous catalyst, showed the highest yield (75.8%) among the basic catalysts tested. The reason can be sought in the strong basicity of CaO. It can be speculated that the active sites favour the abstraction of  $\alpha$ -proton from the ketone molecule at an initial step of the reaction and promote the dehydration at the end of the reaction. However, neither benzyl alcohol nor benzoic acid was observed in the reaction products when CaO was used as a catalyst. It appears that CaO shows a moderate basicity and for this reason suppresses Cannizzaro reaction, which otherwise proceeds under strong basic environment in the condensation reaction [16].

### Effect of Catalyst Amount

To optimize the catalyst amount the reaction was conducted over commercial CaO for 6 h at room temperature with acetophenone/benzaldehyde mole ratio of 1.2 : 1 (Table 1). It can be seen that increased amounts of the catalyst favour enhanced yields of chalcone whereas low catalyst loadings have unfavourable effect. When the amount of CaO was lower than 20%, chalcone in 62.4% yield was obtained, while the yield of chalcone as high as 75.8% was recorded after the catalyst amount was increased to 20%. However, excessive amounts of the catalyst leads to lower yields due to side reactions, such as self-condensation of acetophenone that occurs under moderate concentrations of modified CaO.

### Effect of the Reaction Temperature

The effect of the reaction temperature was investigated using acetophenone/benzaldehyde mole ratio of 1.2 : 1, reaction time of 6 h and 20 wt % CaO. The yield of chalcone increased when the reaction temperature was increased from 30 to 65°C (Table 2). At 30°C a yield of 76.1% was observed and at 60°C 82.3% yield was recorded. With reaction temperatures above 60°C the incremental yield increase was slower than that found for the lower temperature range. Similar effects of increasing temperature on the product yields were reported for Aldol condensation of citral and acetone [17]. Based on the reaction efficiency the optimum reaction temperature of 60°C was chosen for the further experiments.

### Effect of Acetophenone/Benzaldehyde Ratio

To evaluate the effect of reagent concentrations on the yield of chalcone, the reaction was carried out with the acetophenone/benzaldehyde mole ratio varied from 1.1 to 2.0. The results are summarized in Table 3. It can be seen that the yield of chalcone was the lowest with the acetophenone/benzaldehyde ratio of 1 : 1.1 and it increased as the acetophenone/benzaldehyde mole ratio was increased. The highest yield was obtained with a relatively low acetophenone/benzaldehyde ratio of 1 : 1.5 whereas at higher acetone/aldehyde ratios the yields were lower. The results show that commercial CaO is an effective catalyst for the Aldol condensation of acetophenone and benzaldehyde. Since higher acetophenone/benzaldehyde ratio makes a negligible contribution to the yield increase a ratio of 1 : 1.5 was chosen as the optimum acetophenone/benzaldehyde ratio.

### Effect of Modifier Loading

In order to improve the catalytic efficiency of CaO, the surface of calcium oxide was modified and the effect of the modifier loading on the yield of chalcone was investigated at the reaction temperature of 60°C with acetophenone/benzaldehyde mole ratio of 1 : 1.5.

The relevant results are given in Table 4. It can be seen that the catalytic activity of modified CaO increases as the modifier amount increases, and the highest yield of chalcone of 98.9% was obtained with CaO modified by 0.001% bromobenzene. The reason for the high activity of modified CaO should be attributed to the phenyl groups of modifier which formed a hydrophobic layer over CaO surface. Because of structural similarity of modifier and reactants one might expect an increased rate of diffusing reactants to the catalyst surface. Accordingly, more effective performance of the surface active sites results in a higher catalytic activity of modified CaO. However, excessive amounts of the modifier reduce the catalytic activity of modified CaO since modifier molecules can occupy a fraction of active sites on the surface of CaO.

#### Effect of the Nature of Benzaldehyde Substituents

The Aldol condensations of acetophenone with different benzaldehydes over commercial CaO and 0.1% bromobenzene modified CaO were investigated at the optimum reaction condition (20% of the catalyst, 60°C, 6 h). The results are shown in Table 5. It can be concluded that the modified CaO can catalyze the reaction with high rates and excellent yields independent on the nature of aldehyde substituents. Minor differences in the yield of chalcone in the condensation of acetophenone with various aldehydes can be accounted for by different properties of benzaldehyde substituents. The benzaldehydes with strong electron-withdrawing groups ( $-\text{NO}_2$ , entry 2 and 3) are characterized by higher yields. The presence of relatively weak electron-withdrawing groups leads to moderated

**Table 4.** The effect of the amount of bromobenzene in the modified CaO on yield of chalcone in the condensation of acetophenone

Catalyst	Yield of chalcone, %
Commercial CaO	85.8
CaO + 0.5% bromobenzene	86.4
CaO + 0.2% bromobenzene	88.7
CaO + 0.1% bromobzenzene	92.1
CaO + 0.001% bromobenzene	98.9
CaO + 0.00001% bromobenzene	92.7
CaO + 0.000001% bromobenzene	90.6

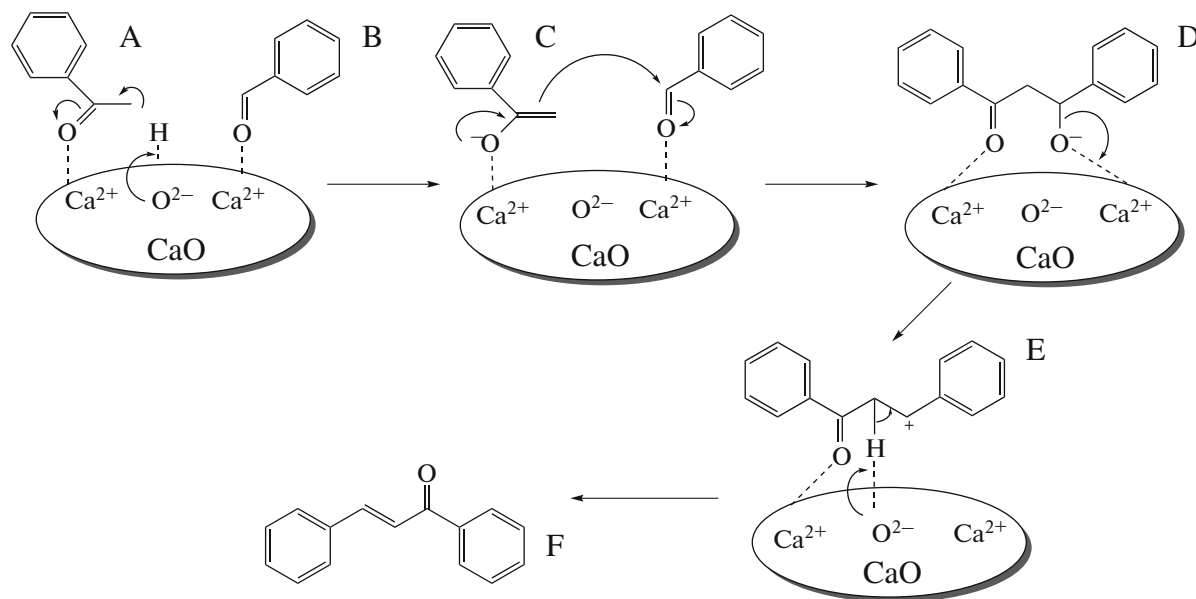
Reaction conditions: 5.0 mmol of acetophenone, 7.5 mmol of purified benzaldehyde/methanol (20 mL), 20% of the catalyst, 60°C, 6 h.

yields, whereas lowest yields were observed with electron-donor groups.

#### Catalytic Mechanism

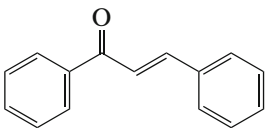
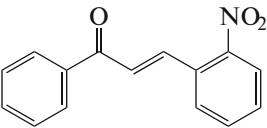
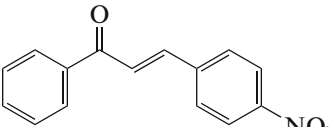
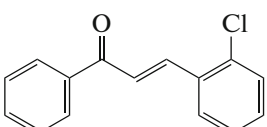
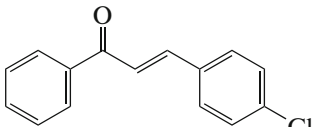
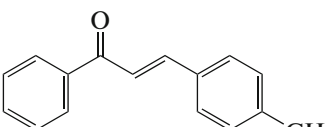
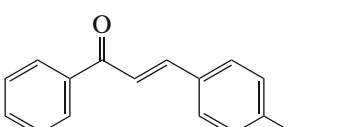
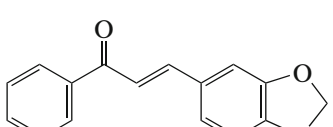
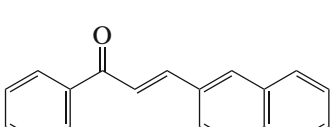
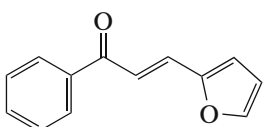
A possible reaction mechanism of Aldol condensation between acetophenone (A) and benzaldehyde (B) over CaO is illustrated in Scheme. According to the scheme, CaO captures a proton and promotes a rearrangement reaction of acetophenone to form C, which is an active intermediate in the Aldol condensation. Through a classical nucleophile attack of C on benzaldehyde, an intermediate D is formed. Then,  $\text{Ca}^{2+}$  ion abstracts an  $\text{O}^-$  from D to form a carbocation E, and finally the deprotonation of E results in the formation of product F.

The possible reaction mechanism of Aldol condensation between acetophenone and benzaldehyde over CaO



**Scheme.**

**Table 5.** Aldol condensation reaction of acetophenone with various aldehydes

Entry	Product	Yield of chalcone, %
1		92.1
2		~100
3		~100
4		94.2
5		95.6
6		92.5
7		90.1
8		90.2
9		94.6
10		97.8

Reaction conditions: 5.0 mmol of acetophenone, 7.5 mmol of purified benzaldehyde/methanol (20 mL), 20% of the catalyst, 60°C, 6 h.

## CONCLUSIONS

In this work, a heterogeneous Aldol condensation of acetophenone and benzaldehyde was effected in the presence of commercial CaO and modified CaO. Results suggest that the commercial CaO is an efficient catalyst for this reaction and by modifying CaO it is possible to significantly enhance the catalytic activity achieving 98.9% yield under the same conditions. The modified CaO have good stability in air attributable to the presence of benzyl groups on the surface of CaO. These groups increase resistance of the catalyst to water and improve adsorption of reactants on the catalyst surface. The best yields of chalcone were recorded for aldehydes with electron-withdrawing groups. The characterization by FT-IR and TG shows that the modifier is attached to surface of CaO by chemical bonds and the hydration of CaO during modifying process is negligible.

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