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Modified calcium oxide as stable solid base catalyst for Aldol condensation reaction

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Abstract. A highly efficient and stable solid-base catalyst for Aldol condensation was prepared by modifying commercial CaO with benzyl bromide in a simple way. It was found that modified CaO can effectively catalyse the Aldol condensation of cyclohexanone and benzaldehyde, as well as various benzaldehydes, to produce 2-benzylidenecyclohexanone with a good selectivity and high yield. Higher yield of 95.8% was obtained over modified CaO after 3 h, which is short compared with the yield of 92.1% after 12 h over commercial CaO. The influence of several reaction parameters, such as temperature, catalyst loading, was investigated. The humidity test over modified CaO reveals that the basic centres of modified CaO are stable for CO_2 and moisture. From the results of Fourier transform-infrared (FT-IR) and Thermogravity analysis (TG) characterization, the modifier was bonded on surface of CaO chemically and almost no $Ca(OH)_2$ formed during the modification process. The type of aldehyde has great influence on the yield of aldol condensation.

Keywords. Aldol condensation; CaO; surface modification.

1. Introduction

Important role of Aldol condensation in the reaction involving C–C bond formation makes it necessary for obtaining many fine chemicals of commercial interest. This kind of reaction can catalytically undergo in the presence of a strong base or acid in liquid phase.[1–3] However, high operating costs and serious environmental issues associated with product separation, purification, corrosion and waste generation attract great efforts toward the development of processes mediated by heterogeneous catalysts. A recent topic of interest in the Aldol condensation is the use of solid base catalysts. Different families of solid bases have been found active in this reaction, including alkali-exchanged zeolites,[4] ion-exchange resins,[5,6] alumina-supported hydroxide,[7,8] Mg–Al hydrotalcites[9,10] and alkaline-earth metal oxides.[11,12] In particular, alkaline-earth metal oxides and hydrotalcite have been regarded as the most potential catalyst for industrial application for its strong basicity and low cost, especially for CaO. However, this solid base has not broadly reached the industrial scene for the technical aspect about the stability of these catalysts upon exposure to moisture air. The basic sites of alkaline-earth metal oxides or hydrotalcite-like samples surface are easy to be poisoned by air due to the adsorption of CO_2 and H_2O on the surface.[13] Furthermore, the single contact between reagents and catalysts causes the catalyst less active than homogeneous strong base, such as sodium hydroxide. Many efforts have been taken towards the activity enhancement of such solid base catalysts by increasing their basicity. The published method for Mg–Al hydrotalcite activation is liquid-phase reconstruction to created surface base sites with uniformly distributed strength as suggested by Ebitani.[14] It should be stressed that all operations during preparation, processing, storage and use of the catalyst was taken extremely carefully in inert gas atmosphere to avoid contacting with air.

Here, the aim of this study is to develop an activated CaO with high efficiency for the Aldol condensation of cyclohexanone and various benzaldehydes with good stability in moisture air. The modifying conditions and various reaction conditions were also investigated.

2. Experimental

2.1 *Modification of CaO*

The surface modification procedure was as follows. Appropriate amount of commercial CaO particles (2.8 g, 100–160 mesh, China National Medicines Co.,

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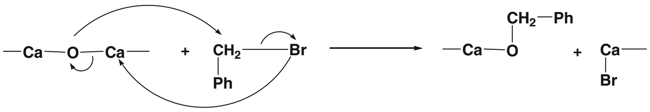
*For correspondence



Scheme 1. The reaction between commercial CaO and benzyl bromide.

Ltd.) were added into the benzyl bromide (Sigma-Aldrich, AR)/methanol solution (40 mL) under stirring at room temperature for activation suggested as in scheme 1. The content of benzyl bromide was varied from 0.01% to 0.5%. After 24 h, the mixture was separated and washed with methanol to remove excess modifier, and the modified CaO was obtained after a vacuum drying process. In order to increase the reproducibility, the particles were sieved before use. Particles of 100–160 mesh size were selected for all experiments.

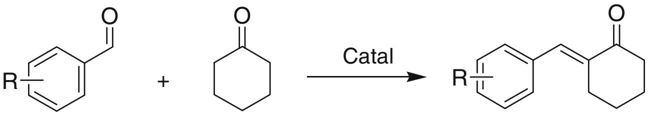
2.2 *Humidity test*

Amount of commercial CaO and modified CaO particles were kept in a container under saturated humidity at room temperature for several days to allow the absorption of water on the surface. The samples were weighed at regular intervals of time. The absorbing moisture rate (%) of the samples was evaluated by the following equation, using the Δm as increase weight, as well as the m_0 as the initial weight.

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

2.3 *Aldol condensation activity test*

As shown in scheme 2, 0.6 mmol cyclohexanone (99%) and 0.5 mmol purified benzaldehyde (99.9%) (molar ratio of benzaldehyde: cyclohexanone = 1.2: 1) were added into 20 ml MeOH in a 50 ml round bottom flask equipped with magnetic stirrer and condenser, and then about 0.25 mmol catalysts was introduced in a constant temperature. The reaction mixture was heated at required reaction temperature ranging from 20 to 65°C at atmospheric pressure. After the completion of reaction, the liquid was cooled and filtrated from the mixture and analysed by gas chromatography using a flame ionization detector and HP-5 capillary column of 30 m length and 0.25 mm diameter, programmed oven temperature of 50–280°C and N_2 (1.5 ml/min) as a carrier gas. The conversion and selectivity were calculated by area normalization method on a carbon basis and the carbon balances are within 100 ± 5% (scheme 2).



Scheme 2. Aldol condensations of cyclohexanone with benzaldehydes.

2.4 *Catalysts characterization*

The Fourier transform-infrared (FT-IR) spectrophotometer (Nicolet Nexus 670, USA) was used to identify the surface group over the catalyst. TGA experiments were carried out using Q600 SDT thermal analysis machine (TA Instruments, USA) under a flow of air in the temperature range from 25°C to 800°C with a ramping rate of 10°C min^{-1}.

3. Results and discussion

3.1 *Humidity test*

For CaO, a water-absorptive material, the poisoning effect of H_2O adsorption during catalyst preparation process are the most important problems to be resolved. The loading of modifier, benzyl bromide, are an important factors for the catalyst moisture absorption rate so to its catalytic activity for Aldol condensation. Too much modifier will lead the catalytic activity to decrease for the occupation of active sites on CaO surface, while fewer modifiers are insufficient for the formation of hydrophobic layer over catalyst surface. Furthermore, the resistance to moisture of the modified CaO will decrease due to a large amount of highly water-absorptive $CaBr_2$ forms when too much benzyl bromide is used over CaO surface. Humidity tests were carried out over various modified CaO with modifier amount in the range from 0.01 to 0.5%. For comparison, the unloaded sample was also included. The tested samples were kept in a vapour-saturated container at room temperature to allow the hydration and carbonation. The weight of each samples were measured at regular intervals of time, and the results were shown in figure 1. It was noted that the moisture absorption rate continues rising for all samples along with time. For the unmodified CaO particles, the moisture absorption rate increases rapidly and reaches to nearly 100% within 50 h, while nearly no weight incensement can be found over modified CaO at the same time, and 0.2% benzyl bromide modified CaO gets the best moisture resistance. It is obvious that the surface modification can improve the moisture resistance of commercial CaO effectively.

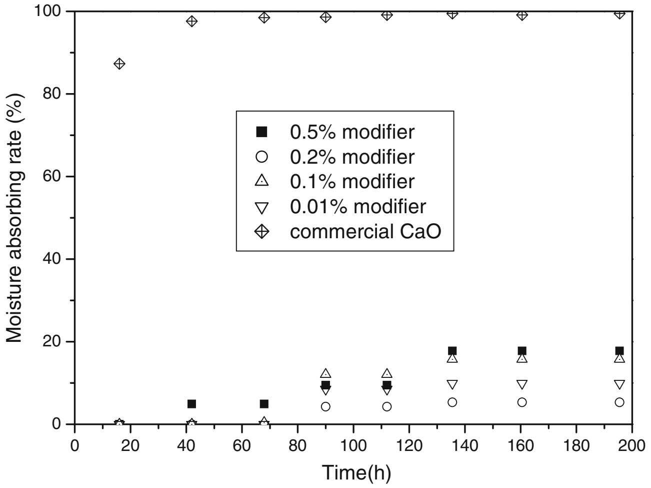


Figure 1. Moisture absorbing rate over commercial CaO and modified CaO with various benzyl bromides.

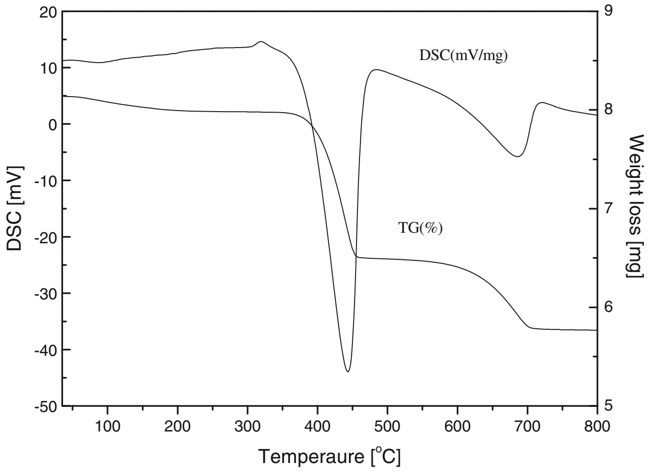


Figure 3. TG/DSC thermogram of modified CaO.

The figure 2 shows the FT-IR spectra of commercial CaO and modified CaO. The spectra display bands at 867 cm^{-1} and 1477 cm^{-1} corresponding to vibration modes of mono and bidentate carbonates. It is also evidenced from the characteristic absorb of C=O between 2000 and 1600 cm^{-1} that indicates the presence of calcium carbonate formed in both catalysts. However, there is no great difference between their intensity, suggesting carbonation by CO_2 in air is very slight over modified CaO. The bands at 1621 and 3460 cm^{-1} are associated with adsorbed water. The important features of the modified CaO appear in the C–H (alkane) stretching (2800–3000 cm^{-1}) and bending (1440 cm^{-1}).[15] The vibration of aromatic carbon double bond bands causes the incensement of intensity at 1600 and 1580 cm^{-1} and the aromatic carbon–hydrogen stretch (3060 cm^{-1}) are evidence of the phenyl groups, which suggesting successful modification over commercial CaO surface.[16]

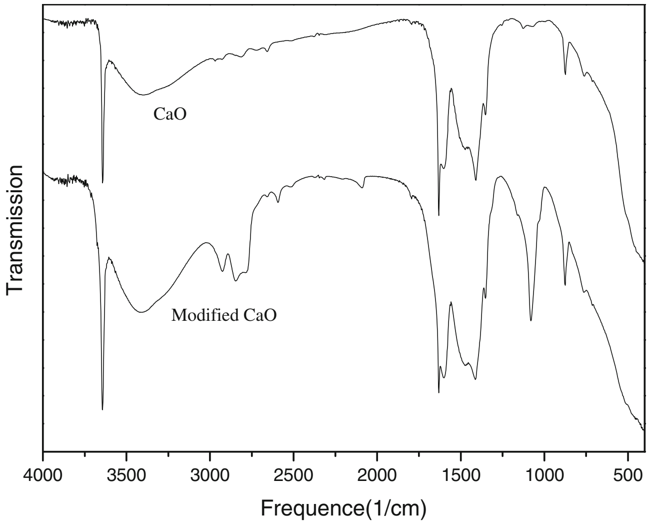


Figure 2. IR pattern of commercial CaO and modified CaO.

Figure 3 shows the TG/DSC thermogravity analysis of commercial CaO and modified CaO. There are two steps in the TG curve in the temperature range from 400°C to 700°C due to the loss of H_2O and CO_2. Furthermore, the DSC curve of the modified CaO presents two broad peaks at 450°C and 700°C corresponding to the decomposition of $Ca(OH)_2$ and $CaCO_3$ formed by the hydration and carbonation of CaO in the storage and preparation. The peaks move to higher temperature range compared with commercial CaO (339°C and 614°C), which indicates the enhancement of thermal stability of modified CaO. Furthermore, from the percentage of weight loss of the two samples, 2.305% for commercial CaO and 2.414% for modified CaO, it can be concluded that the relatively little $Ca(OH)_2$ forms during the modification procedure.

3.2 *Activity comparison of different catalysts*

Particularly, the Aldol condensation can be carried out on homogeneous basic catalysts with good yield and selectivity. A condensation of cyclohexanone and benzaldehyde was operated with kinds of bases at room temperature for 12 h with catalyst amount of 20 wt% as shown in figure 4. From the results, it can be seen that among the homogeneous catalysts the reaction proceed increased with the basicity of catalyst with yield above 30%, and the most efficient catalyst is NaOH. Low catalytic activity for Na_2CO_3 was due to its weak basicity. Surprisingly, CaO showed highest activity of 83.6% yield of 2-benzylidenecyclohexanone among the tested basic catalyst, indicating the basicity of CaO is strong and the most important factor to the active sites to improve the

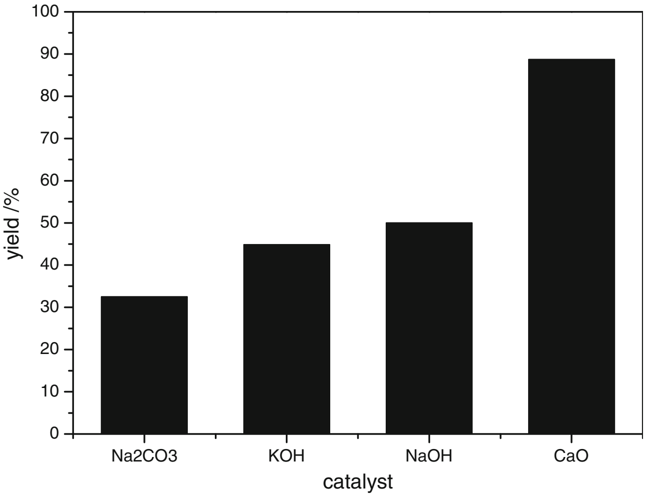


Figure 4. The catalytic performances of various catalysts in Aldol reaction of cyclohexanone and benzaldehyde (catalyst amount = 20%, reaction time = 12 h, cyclohexanone/ benzaldehyde = 1.2: 1, reaction temperature = 65°C).

abstraction of an α–proton form the ketone molecule at the initial reaction and help the dehydration at the end of the reaction.

3.3 *Effect of catalyst amount*

The optimum amount of catalyst was investigated over commercial CaO with reaction time of 12 h at room temperature and cyclohexanone/benzaldehyde molar ratio of 1.2: 1 (figure 5). The yield of 2-benzylidenecyclohexanone increases along with the amount of catalyst. Lower CaO amount (<2%), relatively low yield (36.6%) was observed. On increasing the catalyst amount to 20%, the yield increased up to 94.5%. However, too higher catalyst amount also leads to lower yield due to the decreased selectivity of 2-benzylidenecyclohexanone with the formation of 1,3,5-triphenylpentan-1,5-dione by Michael addition as suggested by Lopez.[17]

3.4 *Effect of reaction temperature*

The influence of the reaction temperature was investigated using a cyclohexanone/benzaldehyde molar ratio of 1.3: 1 and 20 wt% CaO. Yield of 2-benzylidenecyclohexanone was observed due to increase with reaction temperatures ranging from 20°C to 65°C as inferred from figure 6. The results show that a yield of 90.1% at 20°C was obtained after 12 h. With increase of the reaction temperature above 50°C, the incensement of yield is not as high as the change in the low temperature range, which is similar to the results of Aldol condensation of citral and acetone reported by Raju *et al.*[7] The optimum reaction temperature is 65°C for following experiments.

3.5 *Effect of cyclohexanone/benzaldehyde ratio*

To evaluate the effect of reagent concentrations on the yield of 2-benzylidenecyclohexanone, the reaction was carried out with the cyclohexanone/benzaldehyde ratio varied from 1.1 to 2.0. Figure 7 shows that the yield of 2-benzylidenecyclohexanone is the lowest with a cyclohexanone/benzaldehyde ratio of 1:

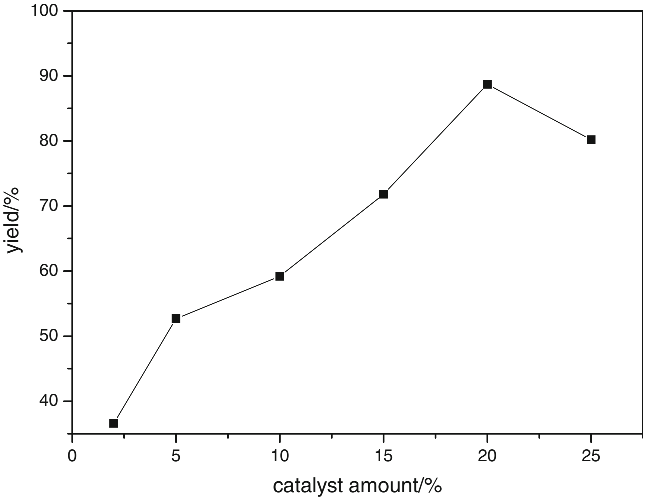


Figure 5. Effects of catalyst amount on Aldol condensation of cyclohexanone and benzaldehyde using commercial CaO as catalyst (reaction time = 12 h, cyclohexanone/benzaldehyde = 1.2: 1, reaction temperature = 65°C).

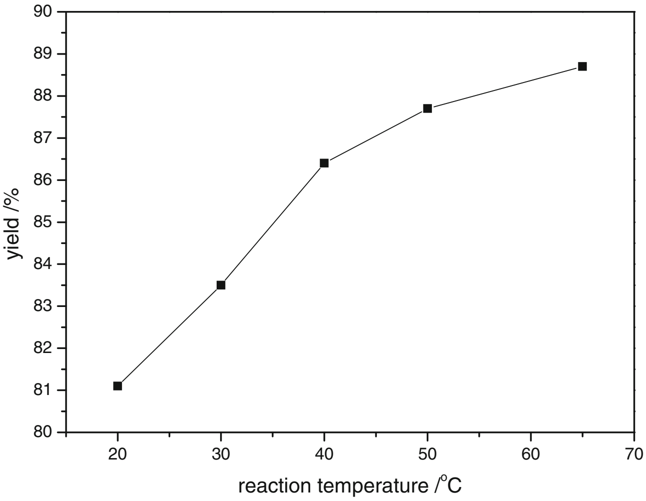


Figure 6. Effect of reaction temperature on Aldol condensation of cyclohexanone and benzaldehyde using commercial CaO as catalyst (catalyst amount = 20 wt%, reaction time = 12 h, cyclohexanone/benzaldehyde = 1.2: 1).

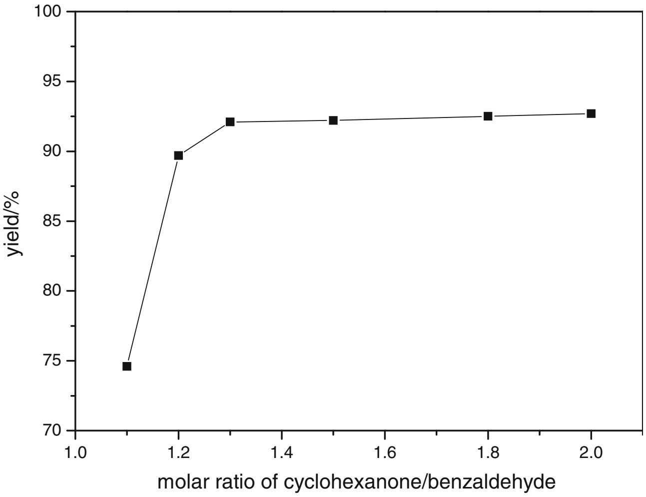


Figure 7. Effect of molar ratio on Aldol condensation of cyclohexanone and benzaldehyde using commercial CaO as catalyst (catalyst amount = 20 wt%, reaction time = 12 h, reaction temperature = 65°C).

1.1. The yield enhances obviously as the cyclohexanone/benzaldehyde ratio increases. The highest yield was obtained with relatively low cyclohexanone/benzaldehyde ratio of 1: 1.3 in comparison with reported high acetone/aldehyde ratio.[1] The results show that commercial CaO is an effective catalyst for the Aldol condensation of cyclohexanone and benzaldehyde. Much higher cyclohexanone/benzaldehyde ratio has increased the yield slightly, so 1: 1.3 was chosen as the optimum cyclohexanone/benzaldehyde ratio.

3.6 *Effect of modifier loading*

The catalytic data over commercial CaO and modified CaO with different amount of benzyl bromide at the reaction temperature of 65°C with cyclohexanone/benzaldehyde molar ratio of 1: 1.3 after 3 h were shown in figure 8. From the results, it can be seen that the time to a high yield of 2-benzylidenecyclohexanone (>94%) was greatly shorted from 12 h for commercial CaO to 3 h for modified CaO. Furthermore, the catalytic activity of modified CaO increases along with the modifier's amount, and the highest activity (94.7% yield of 2-benzylidenecyclohexanone) was obtained over 0.1% benzyl bromide modified CaO. The high activity of modified CaO should be attributed to the phenyl groups forming a hydrophobic layer over CaO surface with similar structure to reactance, which greatly improve the diffusion of reactance to the catalyst surface and make the utilization of active sites over catalyst surface efficient.

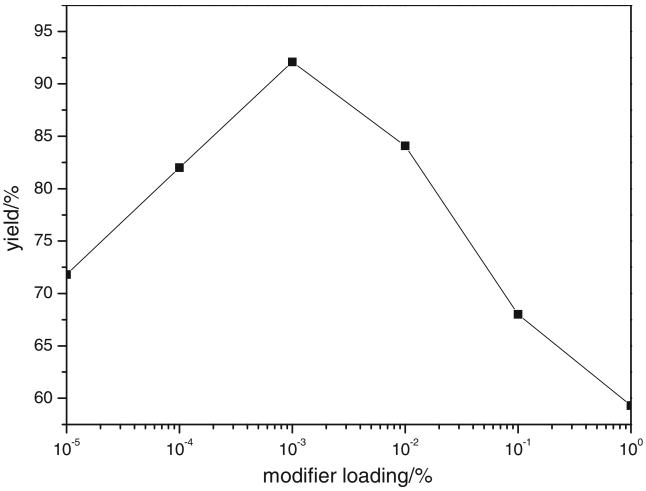


Figure 8. Effect of modifier loading on Aldol condensation of cyclohexanone and benzaldehyde (catalyst amount = 20 wt%, reaction time = 12 h, reaction temperature = 65°C).

3.7 *Catalytic performance over different benzaldehydes*

The Aldol condensations of cyclohexanone with different benzaldehydes over commercial CaO and 0.1% benzyl bromide modified CaO were investigated at the optimum reaction condition (catalyst amount = 20 wt%, reaction time = 3 h, reaction temperature = 65°C) and shown in table 1. From this table, it was found that the modified CaO can catalyse the reaction in a very short time to give high yields, while the yields over CaO are much lower in 3 h, in other word, the modified CaO accelerates this condensation effectively. Further more, we can find the substitutes of benzaldehyde also affect the yield. The benzaldehyde with strong electron-withdrawing groups -NO_2, (entries 1 and 2) give higher yield, but for entry 3 the low yield may be due to the poor selectivity to 2-benzylidenecyclohexanone. Relatively weak electron-withdrawing groups lead to moderated yields and electron-donor groups give lower conversion. Besides, the *ortho* substituted groups lower the yield for the stereochemistry (entries 3, 4, 6, 7, 11).

3.8 *Catalytic mechanism*

The possible reaction mechanism of Aldol condensation between cyclohexanone (**A**) and benzaldehyde (**B**) over CaO was illustrated in scheme 3. In this case, the CaO captures a proton and promotes the rearrangement reaction of cyclohexanone to form **C**, which is an active intermediate of the Aldol condensation. Through a classical nucleophile attacking of **C** to benzaldehyde, intermediate **D** is formed. Then, the Ca^{2+} accept an O^- from

Table 1. Aldol condensations of cyclohexanone with different benzaldehydes.

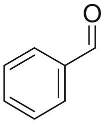
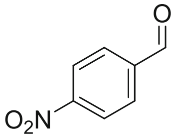
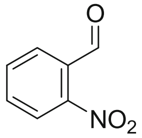
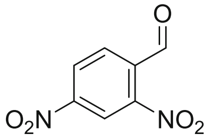
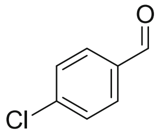
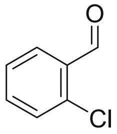
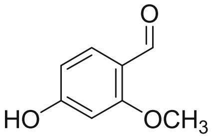
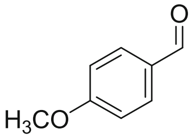
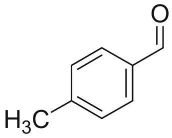
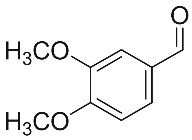
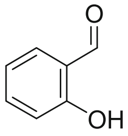
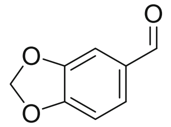
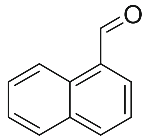
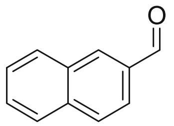
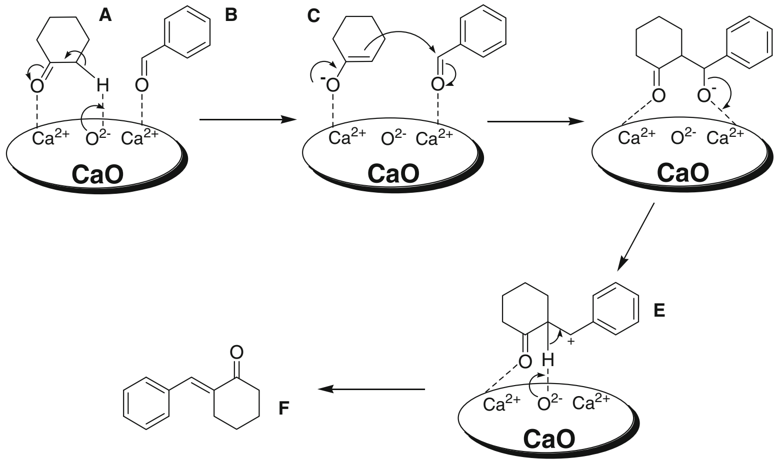
		Yield /%	
Entry	Benzaldehydes	CaO	Modified CaO
1		86.4	95.8
2		85.5	98.5
3		80.2	95.0
4		81.9	92.0
5		81.4	98.6
6		86.4	90.6
7		58.2	83.4
8		81.1	98.8
9		83.5	93.3
10		83.8	91.9

Table 1. (continued).

Entry	Benzaldehydes	Yield /%	
		CaO	Modified CaO
11		48.7	87.0
12		81.2	98.6
13		88.8	99.4
14		89.1	99.1



Scheme 3. The possible reaction mechanism of Aldol condensation between cyclohexanone and benzaldehyde over CaO.

D to form a carbocation **E**, and the deprotonation of **E** results in the formation of product **F** at last.

4. Conclusions

In this work, an efficient catalyst for the Aldol condensation of cyclohexanone and benzaldehyde using commercial CaO and modified CaO as catalysts are shown. It showed that the commercial CaO is an efficient catalyst for this reaction, and the catalytic activity over modified CaO enhances greatly and shortens the reaction time from 12 h to 3 h with an yield of 90% under the same condition. The modified CaO shown good stability in air. It can be attributed to the benzyl groups on CaO surface, which defend the catalyst from water and improve the adsorption of reactance to catalyst surface. The aldhydes with electron-donor group give good yield. The characterization by FT-IR and TG shows that the modifier bonds to surface of CaO chemically and the slight hydration of CaO during modifying process.

Acknowledgements

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