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A Highly Stable and Active CaO/Al_2O_3 Base Catalyst in the Form of Calcium Aluminate Phase for Oxidation of Cyclohexanone to ε-Caprolactone

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Abstract A series of CaO/Al_2O_3 base catalysts with different crystal phases is prepared via thermal treatment. The as-prepared base catalysts are tested through Baeyer–Villiger oxidation of cyclohexanone to ε-caprolactone in liquid-phase using a mixture of aqueous hydrogen peroxide and benzonitrile as oxidant. The corresponding results show that the CaO/Al_2O_3 catalysts with high thermal treatment temperature (e.g. 900 °C) exhibit excellent activity as well as stability. Upon these, the catalysts are characterized by TG–DTG, XRD, N_2-physisorption, SEM and CO_2-TPD techniques. The characterization results clearly suggest that such a stable and efficient catalytic performance is beneficial from the formation of calcium aluminate phase, thus overcoming one of base catalyst application barriers, that Ca or CaO species loss (leach) from CaO-based catalysts during reactions. Correspondingly, it can be inferred that the treatment of the catalysts at different temperatures results in the diverse distribution of basic strength. Furthermore, it is also demonstrated that the suitable base strength (medium strength is good for the reaction selected in the work) plays a critically role in the improvement of catalytic performance. Finally, the effects of operation conditions on catalytic activity and product selectivity are also determined and discussed.

Keywords Solid base catalysts · ε-Caprolactone synthesis · Baeyer–Villiger oxidation · Calcium aluminate

1 Introduction

Heterogeneous catalysts including solid acids and bases are playing an important role with respect to economic and ecological aspects and have been extensively applied in diverse chemical reactions [1–3]. It is noted that the number of processes using sold acid catalysts is overwhelmingly larger than those considering solid bases [4]. In turn, the investigations on solid base catalyst are still receiving great attentions and efforts are devoted for a better understanding of basicity in the solid state aiming to develop new basic materials so as to corresponding industrial processes.

At present, heterogeneous base catalysts have been employed in some typical reactions such as Baeyer–Villiger oxidation [5–8], transesterification and Meerwein–Pondorf–Verley reaction [9–14]. Among the base catalysts used for these reactions, the CaO [9–14], MgO [5], $MgO–Al_2O_3$ [6, 15], hydrotalcite [7, 8] materials have been attracted considerable interests in this context. It is clear that heterogeneous (solid) bases have many advantages over homogeneous catalysts. The former is noncorrosive and environmentally benign as presenting fewer disposal problems, while the latter is difficult in the separation of products and catalysts. However, as far as solid base catalysts are considered, active species in the catalysts such as CaO leaching into the reaction media is always found to be the prime issue [9, 10, 16, 17] in the applications. The drawback

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related to leaching is a big stumbling block to corresponding process development not only the stability thus operational life of the catalysts but also the contamination of products resulting in extra separation burden or lower quality grade of products.

Nowadays, several strategies have been proposed to address this issue in the literatures. Firstly, it is expected that the degree of catalyst leaching can be minimized by controlling the reaction duration. Although reaction duration for a specific conversion could be optimized to include the leaching in consideration, such an optimization is generally shift from the optimization without leaching and has to pay off some amount of product yield as sacrifice. Therefore, another way to resolve the leaching problem is to remove the leached sample after the reaction. Focusing on the leaching problem of CaO-based catalysts, it was reported that leached CaO catalyst from biodiesel can be completely removed by using cation-exchange resin [18]. However, leaching CaO means loss of catalytic activity irreversible and unregenerate, thus the catalysts can only be used in batch processes with low efficiency. While removing CaO via cation-exchange resin is inefficient and also not suitable for bulk production.

It is clear that above strategies on solving problem are the provisional solutions and may only be adapted to some extent in the situation of helpless. The more promising and fundamental settlement is to develop base catalysts having reasonable stability and retain a proper strength of basicity at the same time.

Based on such an aim, stabilizing CaO catalysts by supporting it on appropriate materials or mixing with other metal oxide were investigated. However, it was still observed that there is catalytic species lixiviation into reaction media for CaO mixed with MgO, ZnO as catalysts [10, 19]. Furthermore, since sintering the catalyst at high temperature could reduce the leaching by enhancing the interaction of catalyst components, it was reported that $CaCeO_3$ perovskite catalyst was prepared at high calcination temperature (600 °C). Indeed, the catalyst was endowed with a certain anti-leaching ability. However, a significant decrease in the catalytic activity was found in the fifth reuse, and it was attributed to a remarkable reduction of the number of active sites on the catalyst surface as reported [20]. Another $CaO–CeO_2$ catalyst was prepared by gel formation via a co-precipitation method to enhance the interaction of catalyst components in tandem with the surface properties of the catalyst. However, it was reported that high concentration of leached calcium and cerium species was observed in the first cycle of reaction [21].

In this work, the CaO/Al_2O_3 base catalysts prepared at high calcination temperature to be accompanied with calcium aluminate phase is reported and investigated. Baeyer–Villiger oxidation, feasibly involved with solid base catalysts, is selected as a model reaction, which has evolved into one of the most powerful oxidation routes to convert readily available ketones into more complex and valuable esters or lactones such as ε-caprolactone [22–26].

The CaO/Al_2O_3 catalysts with calcium aluminate phase not only exhibit excellent catalytic activity, but possess outstanding stability in the Baeyer–Villiger oxidation of cyclohexanone in a mixture of aqueous hydrogen peroxide and benzonitrile as oxidant. To the best of our knowledge, there is no prior report for such stable CaO/Al_2O_3 catalysts to be employed in the oxidation reaction.

2 Experimental Section

2.1 Material

Basic alumina (Al_2O_3) (mesh 100–200), 30 % aqueous hydrogen peroxide (30 %, v/v, H_2O_2), calcium acetate ($Ca(CH_3COO)_2{\cdot}H_2O$) (99.5 %), methanol (99.5 %), ethanol (99.5 %) and sodium dodecylbenzenesulfonate (DBS) (99.5 %) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Cyclohexanone (99.5 %) and benzonitrile (99 %) were obtained from Aladdin. All reagents were used as received. The water used in all experiments was deionized water produced by Millipore Milli Q system.

2.2 Preparation of Catalysts

Calcium oxide-supported basic alumina catalysts were prepared by impregnation in the following procedures. Firstly, a calculated amount of calcium acetate ($Ca(CH_3COO)_2{\cdot}H_2O$) was dissolved in a certain amount of deionized water, and stirred at room temperature for half an hour. Afterward, the solution was added dropwise to basic alumina, and impregnating for 24 h. The solid was filtered and collected by washing thoroughly with deionized water and ethanol, and subsequently dried at 110 °C for 3 h to remove residual solvent. The dried catalyst was then calcined in air ambience at required temperature for 2 h. After cooling down to room temperature, the final product are formulated as X % CaO/Al_2O_3-Y °C based on the amount of the catalyst precursor and temperature of calcination, where only $X = 15$ and $Y = (700, 800, 900 \text{ and } 950)$ were reported here. And the basic alumina calcined at 900 °C, represented as Al_2O_3-900 °C, was used as a control. CaO sample derived from calcium acetate, calcined at 900 °C, was also used as a control.

2.3 Catalysts Characterization

The XRD measurements were performed on a Phillips X'Pert Pro Super X-ray diffractometer equipped with

X'Celerator detection system and CuKα radiation (40 kV and 30 mA) was used as the X-ray source. Scans were performed over the 2θ range of 5°–90° with a step size of the 0.0167° and a counting time of 15 s per step.

Nitrogen adsorption–desorption isotherms were conducted by a volumetric adsorption apparatus (Micromeritics Tristar 3000) at −196 °C. Samples were outgassed in vacuum at 300 °C for 3 h before measurements. The surface area of samples was calculated by using the Brunauer–Emmett–Teller (BET) method and the pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) method. The morphology of the samples was obtained by a field-emission scanning electron microscope (FESEM, LEO-1530 Germany).

Thermal-gravity (TG–DTG) measurement was carried out with a TG 209F1 thermal gravimeter. In each test, about 0.30 mg of catalyst was used with the heating rate of 10 °C min^{-1} and the pure air flow rate of 20 mL min^{-1}.

Temperature-programmed desorption of carbon dioxide (CO_2-TPD) was performed on a Micromeritics AutoChem 2920 II instrument. The sample was firstly treated in high purity helium at 400 °C for 1 h, then cooled to 110 °C and saturating with CO_2–helium (10 vol% CO_2) gas mixture at 110 °C for 1 h. The catalyst was purged with high-purity helium at the same temperature. CO_2-TPD was then performed from 110 to 800 °C at a heating rate of 10 °C min^{-1} in the flow. The desorbed CO_2 was detected by using a ThermoStar GSD 301 T2 mass spectrometer at the signal of m/z 44.

2.4 Reaction Conditions

The Baeyer–Villiger oxidation of cyclohexanone was carried out at 70 °C in a 20 mL two-neck flask charged with desired amount of cyclohexanone, benzonitrile, (30 %, v/v) aqueous hydrogen peroxide, sodium DBS and catalyst. One neck of the flask was equipped with a long graham reflux condenser and the other was used for sampling and adding reactants at desired time. The reaction system was vigorously and magnetically stirred. The mixture was cooled down to about 5 °C quickly in an ice-water bath after the reaction finished and the solid was separated from the reaction mixture by centrifugation. The liquid products were analyzed by the flame ionization detector (FID) in a gas chromatography (Shimadzu GC 2010) instrument equipped with a DB-35 60 m × 0.32 mm capillary column and the product identity was confirmed by gas chromatography-mass spectrometry (Shimadzu GC–MS 2010) instrument. For chromatographic analysis, the following temperature program was used: 8 min at 60 °C; 10 °C min^{-1} up to 280 °C; 10 min at 280 °C. Moreover, some of by-products (such as hexanedioic acid) were analyzed by liquid chromatography–mass spectrometry (LC–MS) on a Bruker HCT mass spectrometer. The catalyst was then thoroughly washed with methanol, and dried in a vacuum oven at 60 °C for 2 h for the subsequent stability test experiments.

Table 1 The catalytic performance of CaO/Al_2O_3 catalysts with different calcination temperatures

Catalysts	Conversion (%)	Selectivity (%)	Yield (%)
15 % CaO/Al_2O_3-700 °C	24.8	33.0	8.20
15 % CaO/Al_2O_3-800 °C	36.6	27.8	10.2
15 % CaO/Al_2O_3-900 °C	72.9	100	72.9
15 % CaO/Al_2O_3-950 °C	64.3	100	64.3
CaO	4.20	0	0
Blank-1[a]	0	0	0
Blank-2[a]	0	0	0
Blank-3[a]	52.1	100	52.1

Reaction condition: cyclohexanone 0.15 mL; benzonitrile 1.0 mL; methanol 1.0 mL; surfactant (DBS-sodium dodecylbenzenesulfonate) 0.020 g; reaction time 2.0 h; reaction temperature T = 70 °C; 30 % aqueous hydrogen peroxide 1.0 mL

[a] Compared with the reaction used 15 % CaO/Al_2O_3-900 °C catalyst, Blank-1, 2, 3 represents the reaction without catalyst, benzonitrile, and surfactant, respectively

3 Results and Discussion

3.1 Catalytic Performance of CaO/Al_2O_3 Catalysts at Different Calcination Temperatures

In this section, the catalytic performance of the 15 % CaO/Al_2O_3 catalysts under different thermal treatment temperatures will be discussed. Although other compositions of CaO were studies (demonstrated in Fig. 8), the 15 % CaO/Al_2O_3 is focusing here as the 15 % CaO/Al_2O_3 has much more attractive properties within our studies.

The catalytic performance of the 15 % CaO/Al_2O_3-Y °C catalysts for liquid-phase Baeyer–Villiger oxidation is presented in Table 1. It is clearly observed from Table 1 that calcination temperature significantly influences the catalytic performance, basically showing volcano-type catalytic behavior in the terms of conversion of cyclohexanone and selectivity of ε-caprolactone, especially when the calcination temperature jumped from 800 to 900 °C as the 15 % CaO/Al_2O_3-900 °C and 15 % CaO/Al_2O_3-950 °C catalysts exhibited higher selectivity up to 100 %. In addition, the 15 % CaO/Al_2O_3-900 °C showed highest conversion thus the yield of cyclohexanone. It may also be noted that Baeyer–Villiger oxidation reaction is hardly favorable without catalyst or benzonitrile, while the surfactant is not so important. According to the other report

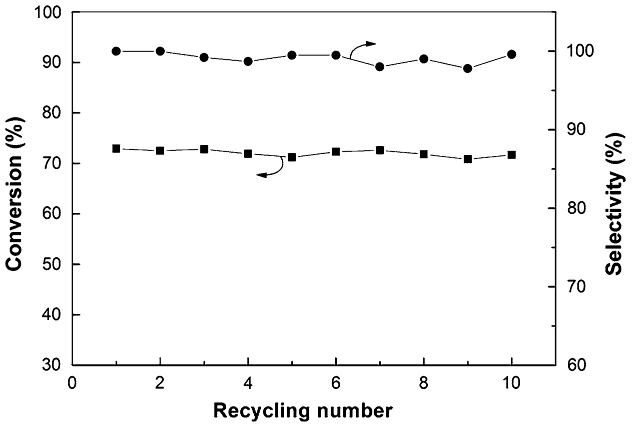

Fig. 1 Stability of the 15 % CaO/Al_2O_3-900 °C catalyst for Baeyer–Villiger oxidation. Reaction conditions: the same as Table 1

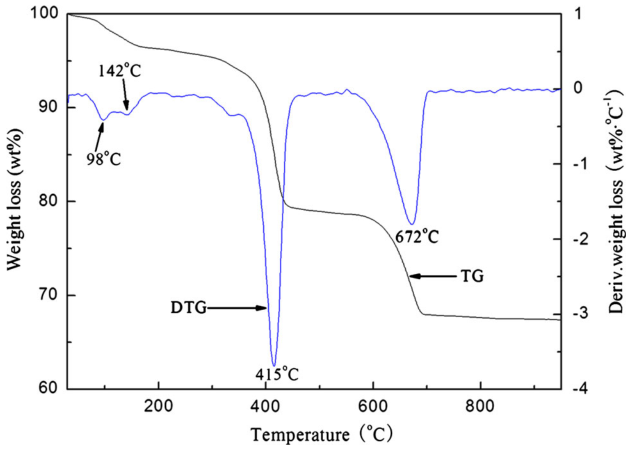

Fig. 2 TG–DTG curves of uncalcined 15 % CaO/Al_2O_3 catalyst

[5], it can be inferred that the longer reaction time may be required to achieve the same conversion when there is no surfactant in the reaction system. Based on these results, it can be concluded that the calcination temperature of 900 °C is appropriate for CaO/Al_2O_3 catalysts in Baeyer–Villiger oxidation, and exhibiting excellent performance in terms of selectivity and activity.

3.2 Recycling the Catalyst and its Stability

The re-use test for the 15 % CaO/Al_2O_3-900 °C catalyst was carried out to determine the stability of the catalyst. Figure 1 shows the catalyst activity change with the reusing cycles (up 10 times in this work) under the reaction conditions in the Baeyer–Villiger oxidation of cyclohexanone to ε-caprolactone. From the profiles of the curves in Fig. 1, it is clear that there is no obvious deactivation of the catalyst in such procedure whatever selectivity or activity. Therefore, it can be concluded that the 15 % CaO/Al_2O_3-900 °C catalyst is fairly stable for this reaction, which is a significant progress for CaO-based catalyst as generally CaO is easy to leach during the reaction in the form of CaO [9, 10].

3.3 TG–DTG Characterization

In order to obtain the decomposition temperature of the precursor ($Ca(CH_3COO)_2 \cdot H_2O$) for the calcination to CaO/Al_2O_3, the thermogravimetric analysis were carried out and the corresponding weight loss of the precursor is presented in Fig. 2. The weight loss for the catalyst can be broadly divided into three regions in terms of temperature. Firstly, the weight loss below 220 °C can be attributed to desorption of physically adsorbed water and crystalline water. Secondly, the weight loss in the region of 350–475 °C can mostly be assigned to the decomposition of calcium acetate, and it is probably also partially for the decomposition of $Ca(OH)_2$ [14]. Thirdly, the weight loss at about 480–700 °C was expected to be the decomposition of calcium salt and produce CaO [27]. Thus, a conclusion can be drawn that the calcium salt precursor can be almost completely decomposed with calcination temperature beyond 700 °C.

Moreover, the high temperature treatment generally exerts a significant effect on the evolution of crystalline phase, which could be applied for these CaO/Al2O3 catalysts. This phase character was further examined by XRD characterization, as described in the following subsection.

3.4 Crystalline Phase Evolution of the CaO/Al_2O_3 Catalysts Under Calcination Treatment

The XRD patterns arising from CaO/Al_2O_3 catalysts under different thermal treatments are displayed in Fig. 3. As shown in Fig. 3b, 15 % CaO/Al_2O_3-700 °C possesses cubic CaO crystal with relatively weak peaks at $2\theta = 32.2$, 37.4, 53.8, 64.2, 67.5, 79.7 and 88.6° [28, 29]. Combined with the fact that there is diffraction peak at $2\theta = 18.1°$ assigned to $Ca(OH)_2$ crystal based on JCPDS 00-044-1481, it can be concluded that CaO particles are relatively well-dispersed on the surface of alumina, and the un-decomposed $Ca(OH)_2$ crystal was expected to be the precursor of CaO to some extent. It can be observed from Fig. 3c that the peaks arising from alumina and CaO crystal become more intense for that of 15 % CaO/Al_2O_3-800 °C catalyst. Hence, it is suggested that the aggregation of isolated alumina and CaO particles takes place. The above-mentioned results also indicate that the interaction between Al_2O_3 and CaO is still relatively weak for those two catalysts under calcination temperature 700 and 800 °C.

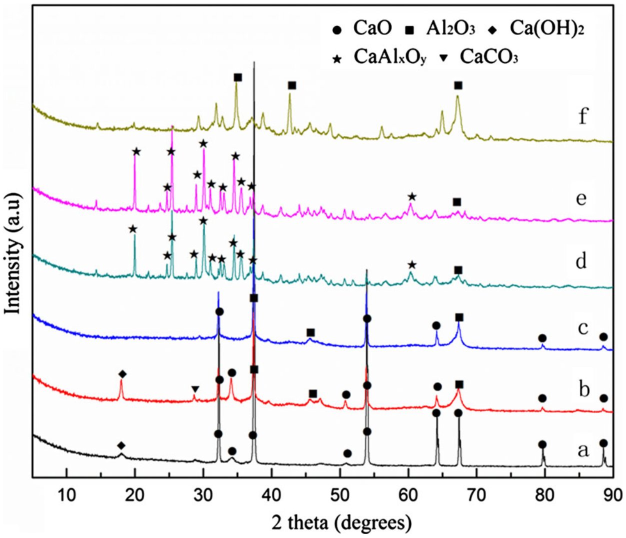

Fig. 3 XRD patterns of CaO (*a*), Al_2O_3 (*f*), and 15 % CaO/Al_2O_3 catalysts calcined at *b* 700 °C, *c* 800 °C, *d* 900 °C and *e* 950 °C

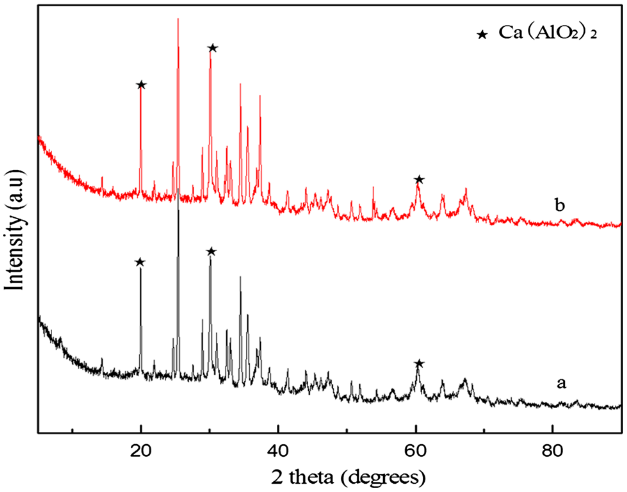

Fig. 4 XRD patterns of the 15 % CaO/Al_2O_3-900 °C catalyst. *a* fresh and *b* used catalyst

However, some significant changes happened when the CaO/Al_2O_3 catalyst was calcined at 900 °C, the peaks arising from alumina and CaO crystal become apparently weaker than that of the 15 % CaO/Al_2O_3-800 °C catalyst (Fig. 3d). More important, it is worth highlighting that new diffraction peaks of calcium aluminate including $CaAl_4O_7$ and $CaAl_2O_4$ appears typically at around $2\theta = 20.0$, 24.7, 25.4, 30.0, 33.0, 34.5, 35.6, 37.3 and 47.3° after calcination according to JCPDS 00-023-1037 and 00-034-0440. Furthermore, it is noted that there is almost no appreciable change of the diffraction peak arising from calcium aluminate phase for the used 15 % CaO/Al_2O_3-900 °C catalyst (Fig. 4). Since CaO-based basic catalyst is often easy to leach during the reaction in the form of CaO [9, 10] resulting in activity loss, the above results strongly suggest that the calcium aluminate phase is quite stable after reaction as it is preventing the loss of Ca species. With higher calcination temperature (950 °C) treatment, one can see that the diffraction peaks of calcium aluminate phase become more intense, while those of alumina phase turns more and more ambiguous (Fig. 3e). It further implies the strong interaction of Ca with alumina species takes place at higher temperature.

Table 2 Textural properties and surface analysis of the catalysts

Catalysts	S_{BET} (m^2 g^{-1})	V (m^3 g^{-1})	r_p (nm)
15 % CaO/Al_2O_3-700 °C	54.5	0.15	4.51
15 % CaO/Al_2O_3-800 °C	50.5	0.12	3.85
15 % CaO/Al_2O_3-900 °C	49.4	0.08	3.26
15 % CaO/Al_2O_3-950 °C	54.1	0.07	2.52
CaO	4.70	0.04	15.2

S_{BET}, V and r_p represent the surface area, pore volume and pore radius of the catalyst, respectively

3.5 Textural Properties of the CaO/Al_2O_3 Catalysts

The pore textural properties of the CaO/Al_2O_3 catalysts determined by nitrogen physisorption are summarized in Table 2. Correspondingly, Fig. 5 depicts the typical nitrogen adsorption–desorption isotherm and the pore size distribution of the 15 % CaO/Al_2O_3-900 °C catalyst. As shown in Fig. 5, the 15 % CaO/Al_2O_3-900 °C catalyst exhibits a typical type-IV nitrogen adsorption isotherm with an additional capillary condensation in the mesopore. It is also evident that the apparent surface area of the CaO/Al_2O_3 catalysts ranges around 50 m^2 g^{-1} even after 950 °C calcination. However, as the calcination temperature increases from 700 to 950 °C, the mesopore radius in these samples decrease from 4.51 to 2.52 nm. It appears that the higher temperature treatment leads to the damage of pore structure, and the foregoing XRD characterization also reveals that the alumina phase is apparently subject to be destroyed after calcination especially beyond 900 °C. It is also consistent with the SEM results, which indicate the aggregation of alumina particles occurs (Fig. 6). A clear exemplification is that apparent surface of alumina decreases from 143 to 33.2 m^2 g^{-1} after calcination (900 °C). Furthermore, the mesopore volume of CaO/Al_2O_3 samples decrease from 0.15 to 0.07 cm^3 g^{-1}. Summarizing with the reaction data in Table 1, it is suggested that the relatively smaller mesopore diameter or volume is not a predominant factor for the catalytic performance of the CaO/Al_2O_3 catalysts.

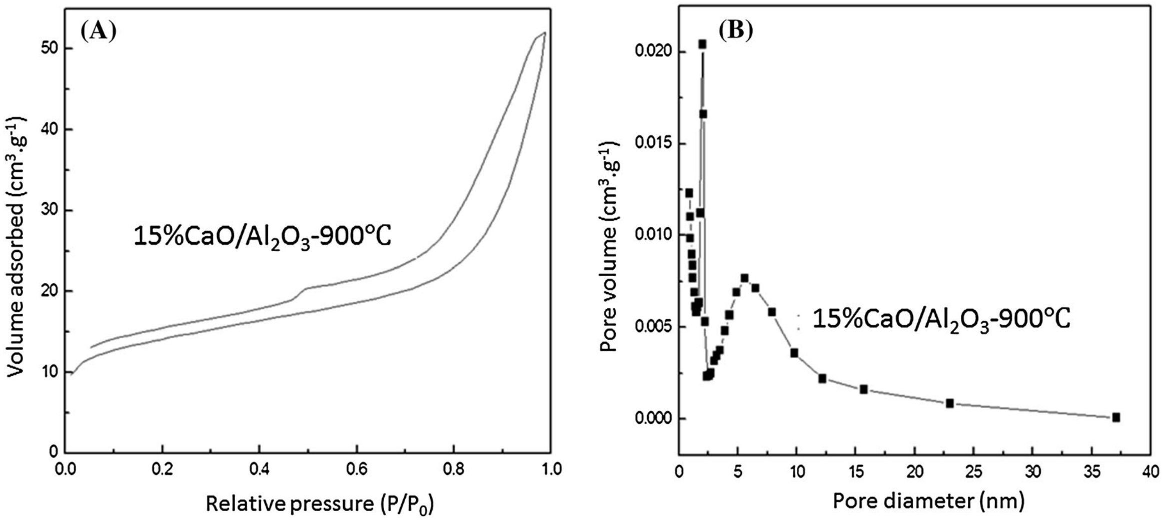

Fig. 5 N_2 adsorption–desorption isotherms and pore size distribution for the 15 % CaO/Al_2O_3-900 °C catalyst

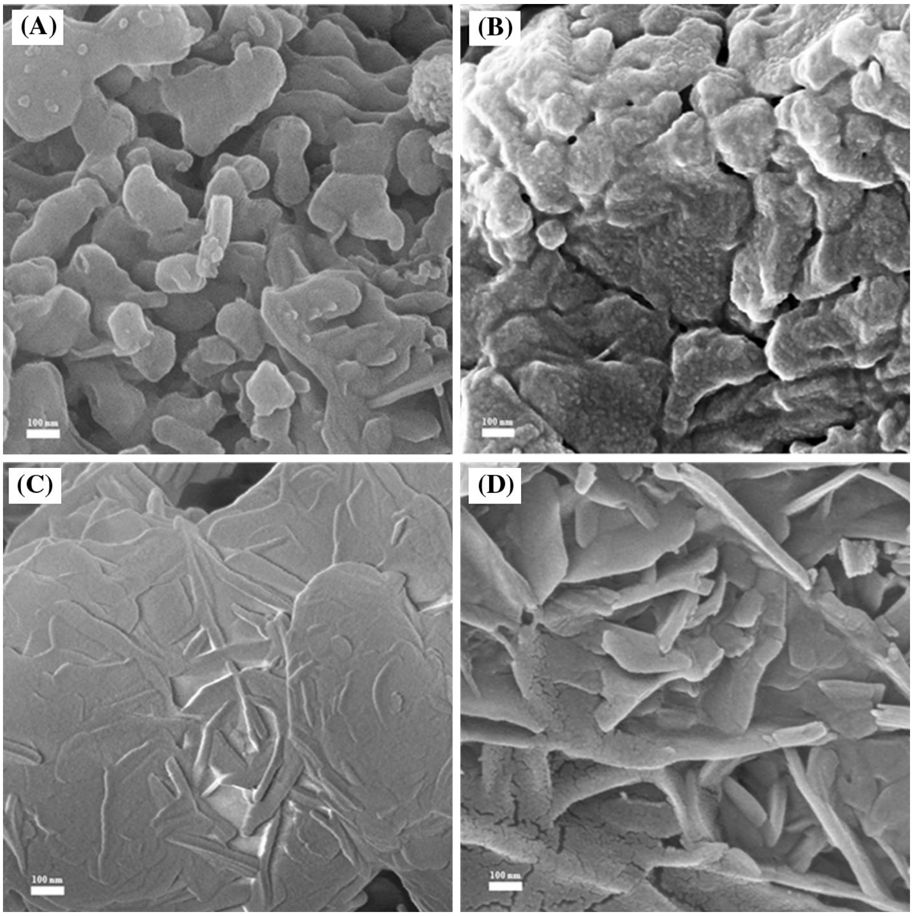

Fig. 6 SEM images of the 15 % CaO/Al_2O_3 catalysts calcined at **a** 700 °C, **b** 800 °C, **c** 900 °C and **d** 950 °C

3.6 Surface Base Properties Correlated with Crystalline of Catalyst

Generally, the different formation of Ca species exerts a significant effect on base strength and quantity, which plays an important role in Baeyer–Villiger oxidation [3]. Thus, the base strength of the CaO/Al_2O_3 catalysts was explored by using CO_2-TPD characterization. Figure 7 illustrates the CO_2 desorption behavior on these catalysts. It can be seen that there is two desorption peaks at different

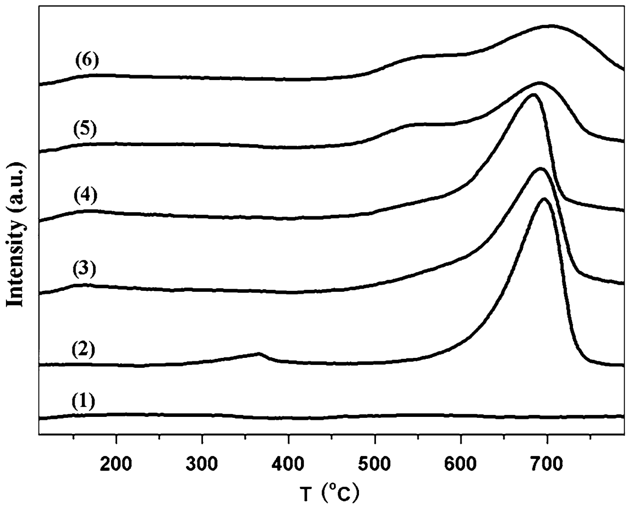

Fig. 7 CO_2-TPD profiles of Al_2O_3 (*1*), CaO (*2*), and 15 % CaO/Al_2O_3 catalysts calcined at *3* 700 °C, *4* 800 °C, *5* 900 °C and *6* 950 °C

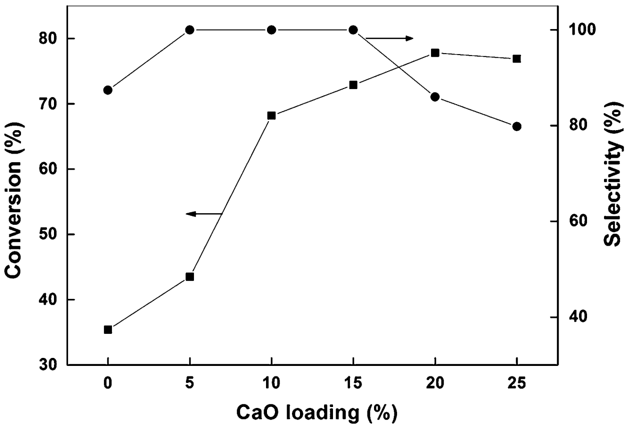

Fig. 8 Effect of CaO loading on oxidation performance for CaO/Al_2O_3-900 °C catalysts. Catalyst: 0.15 g; Reaction time: 2 h; 30 % aqueous hydrogen peroxide: 1.0 mL; DBS: 0.020 g

temperatures for the CaO/Al_2O_3 catalysts calcined below 900 °C, while three desorption peaks appear for the catalysts treated at 900 or 950 °C. Similarly, CaO sample also possesses two desorption peaks around 350 and 680 °C. Since there is no appreciable desorption peak for alumina sample, CO_2 desorption peaks observed are expected to be due to the presence of basic sites with different strengths of calcium oxide present on the surface, subsurface and bulk. Based on the finding of other researchers [30], the desorption peaks around 100 or 350 °C can be attributed to weak base sites which is thought to isolate on the sample surface, while the desorption peaks observed around 550 and 700 °C can be assigned to base sites with medium and strong strength, respectively. It should be noted that only the CaO/Al_2O_3 catalysts calcined beyond 900 °C possess more base sites with medium strength. Combining with their catalytic performance, it can be concluded that the base sites with medium strength play a significantly positive role in the Baeyer–Villiger oxidation. Therefore, the base sites arising from certain species are indeed much important.

Combining these with the aforementioned XRD results, it can be deduced that the weak and strong base sites almost result from calcium oxide isolated in the bulk and those attached to alumina. Although the CaO sample possesses a considerable amount of strong base sites, it just exhibits fairly low catalytic activity. However, when the formation of calcium aluminate phases, the base sites of the catalysts are prone to be in a favorable distribution, which is beneficial for the improvement of ε-caprolactone yield. Furthermore, it seems to indicate that the base sites with medium strength mostly originate from calcium aluminate phase. Therefore, it can be concluded that the active phase of the catalyst is concerned with medium strength base sites, and the suitable amount of these sites is also an important factor for the reaction.

3.7 Optimum Operating Conditions

In the following, experiments were carried out to investigate the effect of CaO loading on oxidation performance for the CaO/Al_2O_3-900 °C catalysts, and the corresponding results are shown in Fig. 8. It can be seen from Fig. 8 that the conversion of cyclohexanone increases with an increase of CaO loading and reached a maximum of 73 % at the 15 % loading. With a further increase in CaO loading, there was a little decrease in conversion but the selectivity of ε-caprolactone increased firstly, and then decreased with the increase of CaO loading. It can be summarized from Fig. 8 that the CaO loading of 15 % is the optimum in terms of the yield of ε-caprolactone.

The effect of reaction time, varied in the range of 1–13 h, on the conversion of cyclohexanone and selectivity to ε-caprolactone was investigated. It can be observed from Fig. 9 that the selectivity to ε-caprolactone was maintained at 100 % for 7 h and gradually decreased afterward, while the conversion of substrate remained the same when the reaction time was more than 7 h. According to previous report [31], it is reasonable to assume that most of 30 % H_2O_2 in the reaction mixture had been fully depleted within 7 h.

The effect of the amount of the catalyst used on the catalytic activity was also studied when the reaction time was maintained at 2 h (Fig. 10). It was demonstrated from Fig. 10 that the selectivity to ε-caprolactone remained unchanged, irrespective of the amount of the catalyst used in reaction, and the conversion of cyclohexanone increased linearly with increasing the amount of the catalyst from

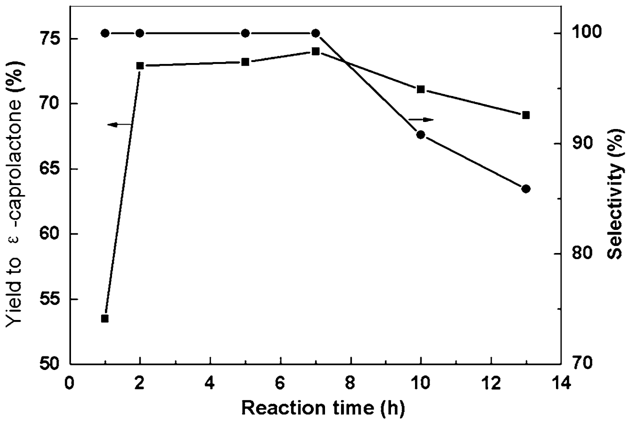

Fig. 9 Effect of reaction time on the catalytic activity. Catalyst: 15 % CaO/Al_2O_3-900 °C, 0.15 g; 30 % aqueous hydrogen peroxide: 1.0 mL; DBS: 0.020 g

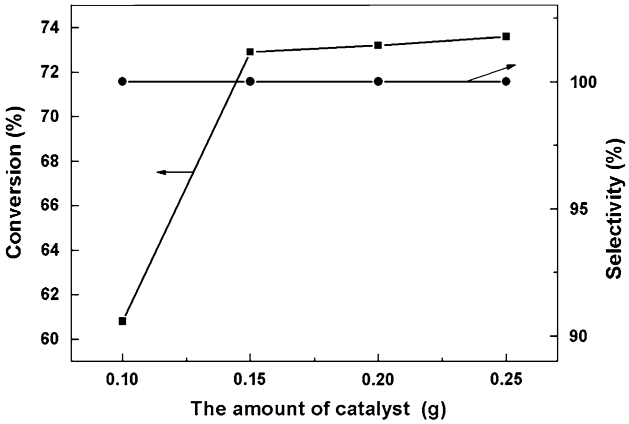

Fig. 10 Effect of amount of the catalyst used on the catalytic activity. Catalyst: 15 % CaO/Al_2O_3-900 °C; Reaction time: 2 h; 30 % aqueous hydrogen peroxide: 1.0 mL; DBS: 0.020 g

0.10 to 0.15 g, but unchanged afterward. Therefore, the optimal amount of catalyst for the Baeyer–Villiger oxidation of cyclohexanone was 0.15 g in this case.

The effect of the amount of 30 % aqueous hydrogen peroxide on reaction was examined and the results are presented in Fig. 11. It can be seen that the cyclohexanone conversion increased with the increase of the amount of 30 % H_2O_2 (oxidant) used, while the selectivity of cyclohexanone to ε-caprolactone was less than 100 % when the amount of 30 % H_2O_2 was above 1.0 mL in volume. And the by-products have been analyzed by liquid chromatography–mass spectrometry (LC–MS) on a Bruker HCT mass spectrometer. They were mainly 6-hydroxycaproic acid and hexanedioic acid. The decline in the selectivity to

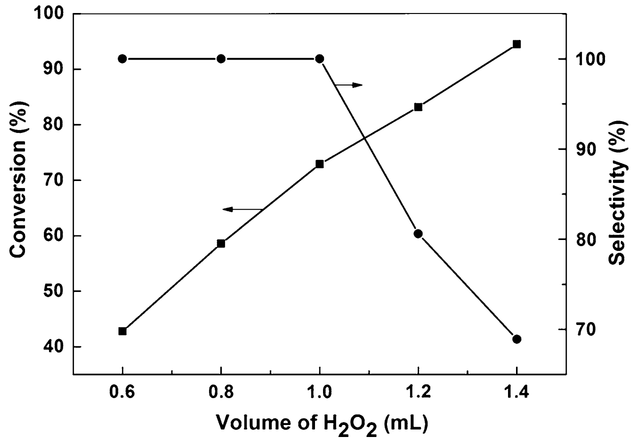

Fig. 11 Effect of the amount of 30 % aqueous hydrogen peroxide on catalytic activity. Catalyst: 15 % CaO/Al_2O_3-900 °C, 0.15 g; Reaction time: 2 h; DBS: 0.020 g

ε-caprolactone may be possibly attributed to the following reasons: (1) as the amount of 30 % H_2O_2 used in the reaction increased, the amount of water in the medium would be more as co-solvent and resulted product, water in this reaction system could cause hydrolysis of the produced esters (ε-caprolactone), dilute and hinder contacts between reagents [31]; (2) the existence of excess hydrogen peroxide in the reaction system resulted in further oxidation of ε-caprolactone to 6-hydroxycaproic acid or hexanedioic acid [32]; (3) the polymerization reaction of ε-caprolactone occurred in this reaction system [33].

4 Conclusions

A simple method with high-temperature treatment has been introduced to prepared CaO/Al_2O_3 catalyst to form calcium aluminate phase. The catalysts treated at high temperature also still possess suitable surface area for Baeyer–Villiger oxidation. Moreover, it strongly suggests that the formation of calcium aluminate phase, being advantageous to prevent the loss of Ca species, substantially leads to a relatively larger amount of base with medium strength. Furthermore, it also demonstrates that the ratio of strong base to those with medium strength (the distribution of base with strong and medium strength) also exerts a significant effect on the catalytic performance. Finally, the optimum operation conditions are achieved as follow: the CaO loading of catalyst 15 %, the amount of catalyst 0.15 g, reaction time 2 h, the amount of aqueous hydrogen peroxide 1.0 mL.

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