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Waste Seashells as a Highly Active Catalyst for Cyclopentanone Self-Aldol Condensation

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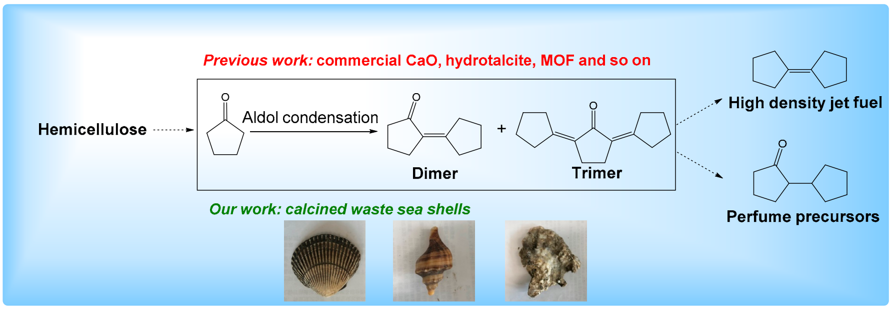
Abstract: For the first time, waste-seashell-derived CaO catalysts were used as high-performance solid base catalysts for cyclopentanone self-condensation, which is an important reaction in bio-jet fuel or perfume precursor synthesis. Among the investigated seashell-derived catalysts, *Scapharca Broughtonii*-derived CaO catalyst (S-shell-750) exhibited the highest dimer yield (92.1%), which was comparable with commercial CaO (88.2%). The activity sequence of different catalysts was consistent with the CaO purity sequence and contact angle sequence. X-ray diffraction (XRD) results showed that $CaCO_3$ in waste shell were completely converted to CaO after calcination at 750 °C or above for 4 h. CO_2 temperature-programmed desorption (CO_2-TPD) results indicate that both the amount and strength of base sites increase significantly when the calcination temperature climbs to 750 °C. Therefore, we can attribute the excellent performance of S-shell-750/850/950 catalysts to the higher CaO content, relatively low hydrophilicity, and stronger acidity and basicity of this catalyst. This study developed a new route for waste shell utilization in bio-derived ketone aldol condensation.

Keywords: biomass; waste seashell; aldol condensation; heterogeneous catalyst

1. Introduction

With the depleting supplies of fossil fuel and increasing environmental problems, the catalytic conversion of biomass to fuel and chemicals has been gaining great attention [1–3]. Compared with other biomass, lignocellulose, which is derived from agricultural waste and forest residues, is much cheaper and more abundant. Therefore, the synthesis of fuel and chemicals with lignocellulose-derived platform molecules has been a research hotspot [4–8].

Cyclopentanone is a promising lignocellulose-derived platform molecule in the conversion of biomass to fuels and chemicals. It can be produced via aqueous-phase selective hydrogenation of furfural derived from hemicellulose [9,10]. Cyclopentanone can undergo a self-aldol condensation pathway, and as-obtained dimer can be used as either high-density fuel [11,12] or perfume precursors [13]. Generally, this reaction was catalyzed by solid base or acid catalysts, for example: commercial CaO, hydrotalcites [11], MOF-encapsulating phosphotungstic acid [14] or MgO-based catalysts [15] (as shown in Scheme 1). However, all of these catalysts need to be prepared by multiple steps or purchased additionally. From the point of view of green chemistry and economic cost, it is still expected to develop bio-based and cost-effective catalysts with high activity for cyclopentanone condensation.



Scheme 1. Reaction pathway of cyclopentanone aldol-condensation.

Waste seashells are one of the major food residues in China, especially in the southeastern coastal areas. The annual production of seafood in China was 35 million tons in 2017. Among these, the production of mollusks was over 12.7 million tons, which accounts for over 36% [16]. Currently, the shells of these mollusks are directly discarded. Thus, using these waste seashells as raw materials for catalyst preparation can not only minimize food residues, but also synthetize cost-effective catalysts. The major constituent of seashells (e.g., clams, conches) is $CaCO_3$, which can be transformed to CaO by direct calcination at appropriate temperatures. In previous work, these calcined waste-shell derived catalysts were mainly employed to produce biodiesel from transesterification of soybean oil [17], palm olein oil [18], etc. In addition, they were also used as pretreatment materials for kraft lignin pyrolysis [19]. However, there is no report about using calcined waste shells as aldol condensation catalysts of bio-derived ketones.

The aim of this paper is to demonstrate the usage of waste seashells as a bio-based and cost-effective catalyst for cyclopentanone condensation with a high activity. Multiple characterizations were also investigated to illuminate the reason for activity differences.

2. Results and Discussion

2.1. Catalytic Activity

Scapharca Broughtonii shell (S-shell), conch shell (C-shell), and oyster shell (O-shell) are three typical waste seashells in Dalian, China, which were chosen as raw materials. After simple pretreatment (calcined at 950 °C for 4 h), three kinds of seashell-derived catalysts were prepared and named as S-shell-950, C-shell-950, and O-shell-950, respectively.

Figure 1 demonstrates the conversion of cyclopentanone and carbon yield of dimer obtained under different catalysts. Among the investigated waste seashell catalysts, S-shell-950 exhibited the best catalytic activity.

From S-shell-950, an 82.2% yield of dimer was achieved, which was comparable with commercial CaO catalyst (88.2%). C-shell-950 also achieved relatively high activity (dimer yield: 82.1%). However, dimer yield of O-shell-950 catalyst was not desirable, which was only 4.6%.

Subsequently, the effect of the S-shell calcination temperature on dimer yield was also investigated (as shown in Figure 2). In the absence of catalyst, no conversion of cyclopentanone was observed. Likewise, no conversion of cyclopentanone was observed if S-shell was used as a catalyst without calcination. However, if we calcined S-shell at different temperatures (e.g., S-shell-550 represents S-shell calcined at 550 °C for 4 h), the catalytic activities showed obviously different: the dimer yield increased significantly when the calcination temperature reached 750 °C, then decreased slightly with the further increment of the calcination temperature. In contrast, trimer can only be detected above 850 °C and the yield of trimer was increased with the further increment of the calcination temperature. Among the investigated catalysts, S-shell-750, S-shell-850 and S-shell-950 exhibited a relatively good catalytic performance. In particular, S-shell-750 catalyst exhibited the best performance; a 92.1% yield of dimer was obtained with nearly 100% selectivity. Moreover, catalyst reusability of commercial CaO and S-shell-950 in this reaction was comparable (as shown in Figure S1). The evidence above indicates that commercial CaO can be substituted directly with S-shell catalysts in this condensation reaction.

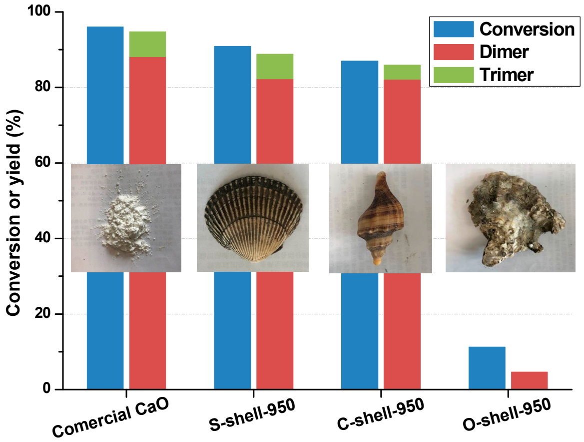


Figure 1. Effect of CaO source on carbon yield of dimer. Reaction conditions: 180 °C; 4.0 g cyclopentanone; 1.0 g catalyst; 2 h.

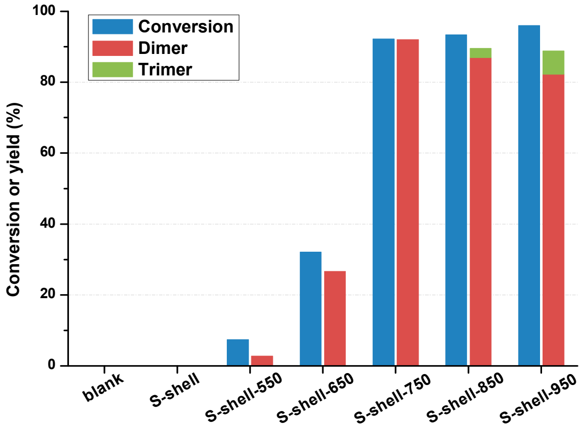


Figure 2. Effect of S-shell calcination temperature on carbon yield of dimer. Reaction conditions: 180 °C; 4.0 g cyclopentanone; 1.0 g S-shell catalyst; 2 h.

2.2. Catalyst Characterization

To get a deeper insight of activity difference of catalysts derived from different sources, multiple characterizations of the catalysts were performed. According to the results of X-ray diffraction (XRD) in Figure 3, the only CaO diffraction peaks were detected after all types of waste seashell calcined at 950 °C for 4 h. This indicates that the $CaCO_3$ ingredient in waste seashell completely converted to CaO at pretreatment conditions (calcined at 950 °C for 4 h).

The Brunauer-Emmet-Teller (BET) specific surface areas of the investigated catalysts were characterized by physical adsorption. As the results shown in Table 1, S_{BET} values of four types of catalysts showed no significant differences, which were around 10 m^2 g^{-1}.

However, the CaO content of these catalysts showed obvious variations (as shown in Table 1). There is an evident correspondence between the activity and the CaO content of catalysts. Among the investigated waste seashell catalysts, S-shell-950 exhibited the highest purity, which is comparable with commercial CaO (97.78% vs. 98.00%). The CaO content sequence for the investigated catalysts was commercial CaO > S-shell-950 > C-shell-950 > O-shell-950, which was consistent with the activity sequence of catalysts mentioned in Figure 1. This result was also confirmed by SEM-EDS (as shown in

Figures S2 and S3 in the supporting information). Compared with S-shell and C-shell, O-shell has more impurity elements (such as Na, Mg, Si, S, Cl), even if calcined at 950 °C.

Table 1. Specific Brunauer-Emmet-Teller surface areas (S_{BET}), CaO content, and contact angle of the calcined shell catalysts.

Catalyst	S_{BET} ($m^2 g^{-1}$) [1]	CaO Content (%) [2]	CA Mean(°) [3]
Commercial CaO	9.69	98.00	16.55
S-shell-950	8.00	97.78	10.42
C-shell-950	11.80	80.34	8.92
O-shell-950	15.73	76.14	5.13

[1]: measured by physical adsorption, [2]: measured by ICP, [3]: contact angle-measured by optical contact angle measurement.

Moreover, the contact angle (CA) of water on the catalyst surface was also measured to evaluate the hydrophilicity of the catalysts (as shown in Table 1 and Figure 4). The CA sequence of catalysts was commercial CaO > S-shell-950 > C-shell-950 > O-shell-950. This sequence was also consistent with the activity sequence of catalysts mentioned in Figure 1. It can be assumed from this result that in this reaction, the activities of CaO catalysts are also related to its hydrophilicity. The more hydrophilic a catalyst is, the lower the activity it obtains. This assumption can be supported by following the literature [20]: CaO catalysts are unavoidably poisoned by atmospheric H_2O or produced H_2O during the reaction. Therefore, if a CaO catalyst is hydrophilic, H_2O can be absorbed by catalyst more easily, which leads to bad catalytic activity. In conclusion, the excellent performance of S-shell-950 catalysts can be explained by two reasons: the high content of CaO and the relatively low hydrophilicity.

Another question to be revealed is the relationship between the calcination temperature and the catalytic activity of S-shell catalysts. As the XRD results in Figure 5a show, when the calcination temperature was below 750 °C, $CaCO_3$ residue was found in S-shell catalysts. When the calcination temperature was raised above 750 °C, no $CaCO_3$ diffraction peak was observed, which indicated $CaCO_3$ was completely transformed to CaO. Figure 5b shows the visible effect of the S-shell with different calcination temperatures. The outside surface of the S-shell transformed from black color to grey color as the calcination temperature increased, which was owing to the decomposition of organism residues. When the calcination temperature was above 750 °C, the calcined shell became fragile and easy to mill into powder. The abovementioned results indicate that $CaCO_3$ in S-shell was completely transformed into CaO after calcination at 750 °C or above.

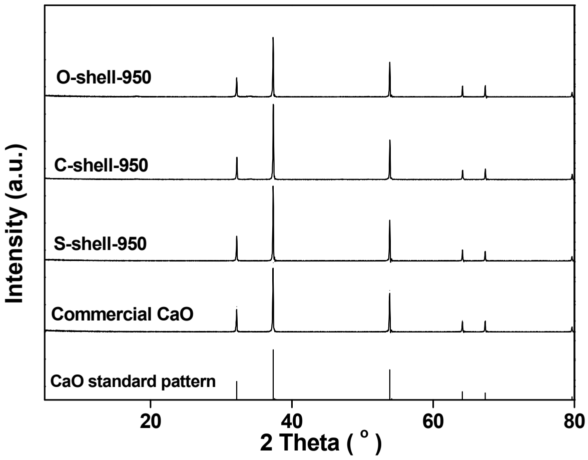


Figure 3. X-ray diffraction (XRD) pattern of commercial CaO and waste seashell after calcined at 950 °C for 4 h.

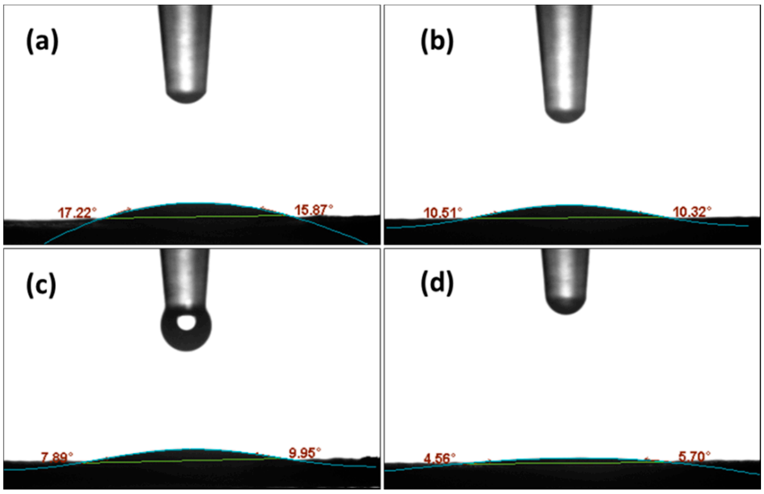


Figure 4. Contact angle of water on catalysts. (**a**) commercial CaO; (**b**) S-shell-950; (**c**) C-shell-950; (**d**) O-shell-950.

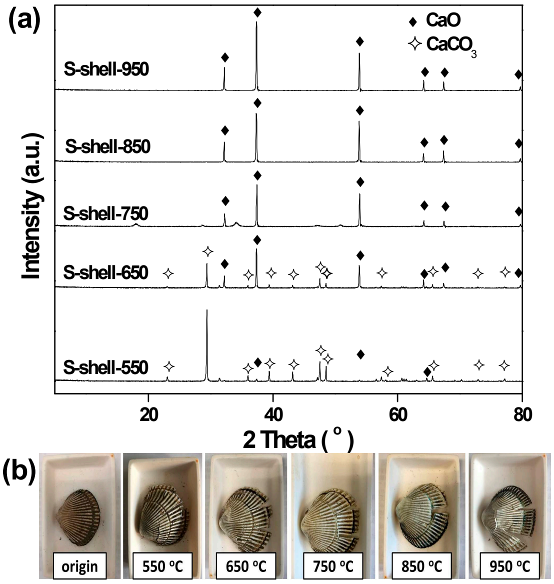


Figure 5. (**a**) XRD pattern of S-shell catalysts. (**b**) The original appearance of S-shell and visible alterations of appearance after calcination at 550–950 °C for 4 h.

In addition, CO_2 temperature-programmed desorption (CO_2-TPD) and NH_3-TPD of S-shell catalysts were also carried out. From the results shown in Figure 6 and Table 2, we can see the calcination temperature has a strong influence on the base sites amount and base strength of the catalysts. When the calcination temperature increased to 750 °C, the amount of base sites and base strength both increased significantly. Likewise, the amount of acid sites was also increased with the increment of the calcination temperature, but the amount was relatively low, which was only ~10 μmol g^{-1}. Among the investigated S-shell catalysts, S-shell-750, S-shell-850, and S-shell-950 catalysts have relatively stronger basicity and acidity. Therefore, we can attribute the excellent performance of S-shell-750/850/950 to the higher CaO content, relatively low hydrophilicity, and stronger acidity and basicity of these catalysts.

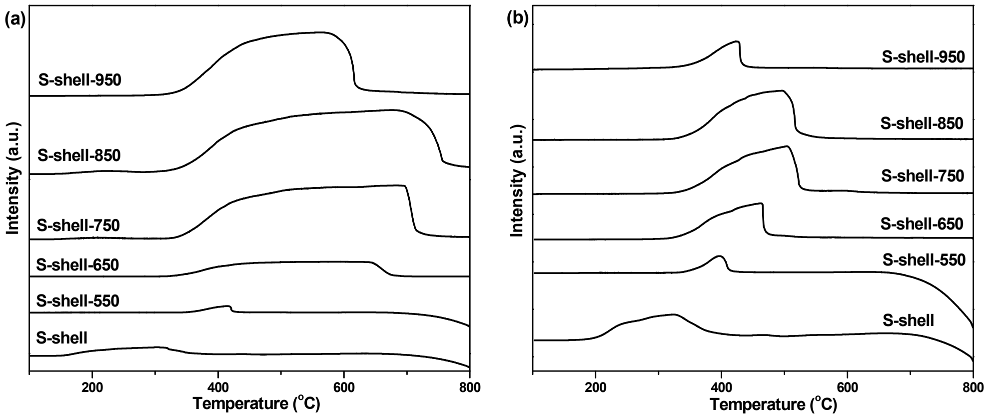


Figure 6. (**a**) CO_2 temperature-programmed desorption (CO_2-TPD) profiles of S-shell calcined at different temperatures. (**b**) NH_3-TPD profiles of S-shell calcined at different temperatures.

Table 2. The amounts of acid sites or base sites of S-shell calcined at different temperatures.

Catalysts	Base Sites Amount (μmol g^{-1})	Acid Sites Amount (μmol g^{-1})
S-shell		
S-shell-550	1.93	2.04
S-shell-650	72.79	9.47
S-shell-750	496.83	16.48
S-shell-850	744.34	14.92
S-shell-950	428.32	5.34

3. Materials and Methods

3.1. Materials and Catalyst Preparation

Waste seashells were collected from home food residue with subsequent washing and drying. Before activity testing, the seashells were calcined in a muffle furnace at the proper temperature for 4 h and milled into powders. Commercial CaO and cyclopentanone were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

3.2. Characterization of Catalysts

3.2.1. X-ray Diffraction (XRD)

XRD patterns of different CaO catalysts were recorded with a Shimadzu X-Ray diffractometer XRD-6100 from Shimadzu, Japan, using Cu target at a scan speed of 5° min^{-1}. Before tests, the CaO catalysts were calcined at the required temperature for 4 h in a muffle furnace.

3.2.2. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

The actual CaO contents in catalysts were measured by ICP-OES (Perkin-Elmer Optima 8000, Waltham, MA, USA). Before tests, the different CaO catalysts were calcined at 950 °C for 4 h. Based on the Ca contents, the CaO contents were calculated as follow:

$$\text{CaO content} = \frac{\text{Ca content}}{\text{M(Ca)}} \times \text{M(CaO)} \times 100\%$$

M(Ca): 40.0; M(CaO): 56.0

3.2.3. Physical Adsorption

The specific Brunauer-Emmet-Teller surface areas (S_{BET}) of the CaO catalysts were measured by nitrogen physisorption at 77 K using an ASAP 2020 PLUS HD88 apparatus (Micromeritics, Norcross, Georgia, USA). Before the measurements, the samples were evacuated at 573 K for 3 h.

3.2.4. Chemi-Sorption

The basicity of S-shell catalysts was characterized by CO_2 temperature-programmed desorption (CO_2-TPD) experiments on a PCA-1200 chemi-adsorption analyzer provided by Biaode electronic technology CO.,LTD (Beijing, China). For each test, the sample was placed in a quartz reactor, pretreated in He flow at its preparation temperature for 1 h, and cooled down in He flow to 80 °C. After the saturated adsorption of CO_2, the sample was purged with He at 80 °C for 45 min to remove the physically adsorbed CO_2. The desorption of CO_2 was carried out in He flow from 80 °C to 800 °C at a heating rate of 10 °C/min.

The acidity of the solid base catalysts was measured with NH_3-TPD on the same catalyst characterization system as we used in CO_2-TPD. For each test, the sample was placed in a quartz reactor. Before the measurement, the sample was purged with He flow at 120 °C for 2 h. After the saturated adsorption of NH_3 at 120 °C, the sample was maintained at 100 °C in He flow for 45 min to remove the physically adsorbed ammonia. The desorption of NH_3 was conducted in He flow from 100 °C to 800 °C at a heating rate of 10 °C/min.

3.2.5. Contact Angle

The contact angle (CA) of water on catalyst surface was observed by Biolin Scientific Attension® Theta Flex (Gothenburg, Sweden).

3.2.6. Activity Test

The self-aldol condensation of cyclopentanone was conducted in a 20 mL stainless steel batch reactor with Teflon lining. Typically, 4.0 g cyclopentanone and 1.0 g catalyst were used. Before each reaction, the reactor was purged with nitrogen for 30 s. Then the reactor kept stirring at 180 °C for 2 h. After the reaction, the reactor was quenched to room temperature with water. The products were taken out and dissolved in 96 g 1% cyclohexanone (internal standard)—ethanol solution. The solution was filtrated, diluted with ethanol, and analyzed by a Varian 450-GC. Before the test, the catalysts were calcined at the required temperature.

4. Conclusions

CaO catalysts derived from three types of waste seashell were first reported as active catalysts in cyclopentanone self-aldol condensation. Among the investigated catalysts, S-shell-750 catalyst exhibited the highest catalytic activity and selectivity (dimer yield: 92.1%; selectivity: up to 100%), which was comparable with commercial CaO (dimer yield: 88.2%). According to the results of multiple characterizations, the excellent catalytic performance of S-shell catalysts can be rationalized by its relatively higher CaO content, low hydrophilicity, and stronger basicity/acidity. In this reaction, commercial CaO can be substituted directly by S-shell-750 catalyst. This work developed a new route for using cost-effective bio-based catalysts for biomass platform chemical conversion.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/8/661/s1, Figure S1: Catalyst reusability of commercial CaO and S-shell-950 catalysts. Reaction conditions: 4.0 g cyclopentanone; 1.0 g catalyst; 180 °C; 2h. Catalysts were regenerated by calcination at 950 °C for 4 h. Figure S2: SEM-EDS data of catalysts before calcination. (a) commercial CaO; (b) S-shell; (c) C-shell; (d) O-shell. Figure S3: SEM-EDS data of catalysts after calcination at 950 °C. (a) commercial CaO; (b) S-shell-950; (c) C-shell-950; (d) O-shell-950.

Author Contributions: X.S. conceived and designed the experiments; Q.X. and X.W. performed the experiments; N.L., H.J., M.N. and H.S. analyzed the data; J.Z. and Q.P. contributed reagents and analysis tools; X.S. wrote the paper.

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Conflicts of Interest: The authors declare no conflict of interest.

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