# Eco Friendly Egg Shell Mediated Aldol Condensation

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**Abstract:** We reported the egg shell as a cheap, environmentally benign catalyst for aldol condensation. This clean protocol is employed to prepare variety of chalcones, resulted in good yields with short reaction time. This method has advantages over homogeneous catalyst <sup>1,2</sup> such as sodium hydroxide, potassium hydroxide, amines, ammonium or ammonium salts and pyridine which are highly toxic and corrosive.



The catalyst is reusable even after fifth run with good yield. XRD, SEM and UV-DRS spectra of egg shell membrane (ESM) proves the presence of crystalline and heterogeneous nature of  $CaCO_3$ . Here, we report the ESM, as an inexpensive, easily available, reusable, solid support for calcium carbonate with high catalytic activity for the synthesis of chalcones, under mild reaction condition.

Keywords: Egg-shell membrane, heterogeneous catalyst, Ethanol, chalcones, green chemistry, Aldol condensation.

# 1. Introduction

A traditional concept in process chemistry has been the optimization of the time-space yield. From our modern perspective, this limited viewpoint must be enlarged, as for example toxic wastes can destroy natural resources and especially the means of livelihood for future generations. In addition, we must ensure that future generations can also use these new alternatives. "Sustainability" is a concept that is used to distinguish methods and processes that can ensure the long-term productivity of the environment, so that even subsequent generations of humans can live on this planet. Sustainability has environmental, economic, and social dimensions.

#### 1.1 Calcium Carbonate

Calcium carbonate is a common substance found in rocks, shells of marine organisms, snails, coal balls, pearls, and eggshells. Calcium carbonate is the active ingredient in agricultural lime, and is usually the principal cause of hard water. It is commonly used medicinally as a calcium supplement or as an antacid, but excessive consumption can be hazardous.

# **1.1.1 Chemical Properties**

It reacts with strong acids, releasing carbon dioxide. It releases carbon dioxide on heating (to above 840 °C in the case of CaCO<sub>3</sub>), to form calcium oxide, commonly called quicklime, with reaction enthalpy 178 kJ / mole:



#### 1.1.2 Uses - Industrial Applications

The main use of calcium carbonate is in the construction industry, either as a building material or limestone aggregate for road building or as an ingredient of cement or as the starting material for the preparation of builder's lime by burning in a kiln. It is also used as a food additive, as an acidity regulator, anticaking agent, stabiliser or colour. <sup>5,6</sup> It is used in some soy milk products as a source of dietary calcium. Calcium carbonate is also used as a firming agent in many canned or bottled vegetable products.

# 2. Results and Discussion

The aldol addition reaction is recognized as one of the most fundamental tools for the construction of new carbon– carbon bonds in both the biochemical and purely chemical domains.

The traditional aldol condensation involves the use of sodium hydroxide, potassium hydroxide, pyridine and other nitrogenous bases are highly toxic and corrosive. The replacement of such reagents is impossible as it dissolves with the products. So the product separation is very difficult and expensive. Moreover, the main drawbacks of homogeneous process include lack of recycling of the catalyst and post reaction work-up of spent liquid bases. Therefore, it is desirable to develop solid base catalysts to overcome these disadvantages and provide a commercial process having the potential of easy handling of the catalyst, easy separation of products, and lower corrosion in the reactor, producing the desired product with high selectivity and possible regeneration and reuse of the catalyst. So in this present study, we employed eco-friendlier, less- expensive, easily available egg shell, calcium carbonate source as a heterogeneous catalytic agent for aldol reaction.

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#### 2.1 Optimization of the Catalyst

 Table 1: Synthesis of 4-hydroxy-4-phenylbutan-2-one with various catalyst.<sup>a</sup>

S. No	Catalyst	Solvent	Time (min)	Yield(%) <sup>b</sup>	
1	NaOH	Ethanol	30	85	
2	KOH	Ethanol	40	79	
3	CaCO <sub>3</sub>	Ethanol	40	83	
4	Na <sub>2</sub> CO <sub>3</sub>	Ethanol	90	25	
5	Egg shell	Ethanol	20	85	
6	Egg shell	CHCl <sub>3</sub>	60	45	
7	Egg shell	C <sub>2</sub> H <sub>5</sub> COOCH <sub>3</sub>	60	33	
8	Egg shell	Water	90	20	
9	Egg shell	No solvent	90	25	
<sup>a</sup> Benzaldehyde (1 mmol); Acetone (1 mmol); Ethanol;					
catalyst (10mg), R.T, <sup>b</sup> Isolated yield					

To identify the best catalyst, the catalytic activities of various catalysts were investigated for the synthesis of aldol under our experimental conditions. The results including the percentage yield were summarized in Table.1. Among the various catalysts studied, though the best yield was obtained with NaOH. The catalysts KOH and CaCO<sub>3</sub> too resulted in good yield of aldols. As egg shells being eco-friendlier waste was utilized as a "GREEN CATALYST" which resulted in a very good yield with short reaction time. To the study the solvent effect, the reaction was carried out without solvent and with different solvents such as CHCl<sub>3</sub>,  $C_2H_5COOCH_3$  and water. Poor results were obtained when the reaction carried out in solvent Free State and in water. When the reaction was carried with CHCl<sub>3</sub> and  $C_2H_5COOCH_3$  too resulted in poor yield

 Table 2: Reusability of egg shell in the synthesis of aldol<sup>a</sup>

Run <sup>b</sup>	First	Second	Third	Fourth	Fifth		
Yield (%)	80	77	76	76	75		
<sup>a</sup> Reactions		are	perform	ned	with		
Benzaldehyde(1mmol); Acetone (1mmol); Ethanol							
catalyst (10mg). <sup>b</sup> After completion reaction, catalyst							
was filtered and washed thrice with acetone, air dried,							

As recyclability was important for industrial application of a catalyst, the reuse performance of egg shell was investigated. It was noteworthy that the recovered catalyst was recycled by filteration and drying in air. After fifth cycle exhibited the comparable consistent activity with 75% yield.

# 2.2 Characterization of the Compound

#### 4-hydroxy-4-phenylbutan-2-one

This compound is prepared according to the general procedure and recrystalized from ethanol to give white solid (90% yield).



**M.P.:** 168-170°C.

**UV-Vis. (EtOH)** λ<sub>max</sub>: 230, 329, 331, 341 nm.

**FT-IR (KBr)** γ cm<sup>-1</sup>: 3315.41, 3176.54, 1649.02, 1593.09, 1396-37, 1191.93, 1114.78, 983.63, 756.04, 653.82, 603.68





one

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2.3 Characterization of the Catalyst, Egg shell



Figure 2.3: XRD of the catalyst-egg shell, CaCO<sub>3</sub>



Figure 2.4: SEM image of the catalyst egg shell, CaCO<sub>3</sub>

An egg shell, CaCO<sub>3</sub> was characterized by powder XRD, SEM and UV-DRS spectra. X-ray powder diffraction pattern for CaCO<sub>3</sub> was shown in Figure 2.3. The structure of CaCO<sub>3</sub> is retained as observed from the retention of all the characteristic peaks in XRD. The diffraction patterns of the CaCO<sub>3</sub> samples show the reflections in the range 5-50° typical of zeolites. The sharp intense peaks at 29.49°, 47.63° and 48.60° show the good crystalline nature of the CaCO<sub>3</sub> material.



SEM image shown in Figure 2.4 suggests that CaCO<sub>3</sub> is highly dispersed. The calcium was confirmed by the absorbance at 234 nm and 289 nm of egg shell in UV-DRS

#### 3. Experimental Section

spectra.

#### 3.1.1 Determining the Calcium Content of the Catalyst-Eggshells

Calcium carbonate is a component of seashells and eggshells that gives them their strength and hardness. When calcium carbonate reacts with hydrochloric acid, the products are carbon dioxide, water, and calcium chloride. Hydrochloric acid is added to an eggshell to dissolve all of the calcium carbonate in the shell. The portion of the eggshell that is not calcium carbonate does not react with the acid and remains as solid. The solid parts of the eggshell are separated from the calcium carbonate by filtration. The filtrate is used to determine the percentage of the eggshell that contains calcium carbonate.

#### Procedure

The pieces of eggshells were crushed. The eggshell was transfer to a 250 ml beaker and its mass was recorded. 45 ml of 1.0 M HCl was added to the eggshells and stirred with a glass rod until air bubbles ceased. A dry filter paper was weighed for filtration. The dissolved eggshell was poured through the filter paper. The filtrate was washed with a little deionized water. The filtrate was dried and its mass was recorded.

# Calculations

The mass of the filtrate was calculated by subtracting the mass of the filter paper from the mass of the filtrate and the filter paper. The mass of the calcium carbonate was calculated by subtracting the mass of the filtrate from the mass of the eggshell. The percent of calcium carbonate in the eggshell was calculated by dividing the mass of calcium carbonate by the mass of the eggshell and then multiplying by 100. The number of moles of calcium carbonate in the sample was calculated

Table 3: Calculation of % of CaCO <sub>3</sub>	in egg shell
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Mass of the content	Eggshell
Mass of eggshell	2.788g
Mass of filter paper	1.010g
Mass of filter paper & unreacted eggshell	1.651g

#### **3.1.2 Preparation of Aldol Procedure**

7.5 ml ethanol and 10 mg egg shell was placed in a 10-ml test tube, and stirred at room temperature in a mechanical stirrer. A mixture of 1.4ml fresh benzaldehyde and 0.5ml acetone were added to the test tube. Then, the solution was stirred for further 10 minutes. After completion of reaction the catalyst was filtered and the filtrate was concentrated to get the recrystrallized product without further purification. The filtered catalyst was washed with water and dried at room temperature and used for further run and its reusability was checked.

#### 3.1.3 Weight and Melting Point Determination of 4hydroxy-4-phenylbutan-2-one

The melting point of the products was recorded. The yield and TON are noted.

# 3.1.4 Characterization

The prepared aldols were characterized by comparing its melting points with authentic samples 4-hydroxy-4-phenylbutan-2-one was characterized by UV-Vis, IR and1HNMR spectral data.

# 3.1.5 Instrumentation and other methods of analyses

Aldol was characterized by <sup>1</sup>HNMR and <sup>13</sup>CNMR (Brucker 400 MHz) spectral techniques using CDCl3 with TMS as an internal standard. Optical densities were monitored at appropriate wavelengths ranging from 190-600 nm in aqueous medium in UV-Vis spectrophotometer (JASCO V-550 double beam spectrophotometer with PMT detector). The XRD pattern of the catalyst samples is measured with a PW3050/60 (XPERT-PRO Diffractometer

system) instrument using a Cu K $\alpha$  radiation at room temperature.

# 4. Conclusions

Aldol condensation reactions of aldehydes and ketones are widely used in organic synthesis to prepare chemicals containing double bond conjugated with a carbonyl group. Inorganic solids and solid-supported reagents, such as amino group immobilised on silica gel, clays, magnesium and aluminium oxides, zeolites, were used, such compounds provided operational simplicity and higher selectivity with the possibility of using. Recently solid basic catalysts received increased attention as they facilitate a variety of organic reactions that take place via carbanionic intermediates.

The traditional aldol condensation involves the use of sodium hydroxide, potassium hydroxide, pyridine and other nitrogenous bases are highly toxic and corrosive. So in our present study, we employed eco-friendlier, less- expensive, easily available egg shell, calcium carbonate source as a catalytic agent for aldol reaction.



The egg shell, Calcium carbonates mediated aldol condensation has *several advantages as a "catalyst"*: Easy availability, Eco-friendlier, Less expensive, Readily separated by filtration, Reusable and recyclable. This **method of synthesis** of aldol using egg shell as a **catalyst** involves has **many advantages** such as simple experimental procedure, mild reaction condition, No chemical wastes, Short reaction time, Good yield, Atom economical. The egg shell contains CaCO<sub>3</sub> and its XRD of its proves the crystalline and heterogeneous nature. This catalysts show very high activities and possess the potential to be reused several times

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