

POTASSIUM CHLORIDE IMPREGNATED ON ACTIVATED GREEN MUSSEL SHELLS (KCl/AGMS): AN ACTIVE CATALYST TOWARDS KNOEVENAGEL CONDENSATION

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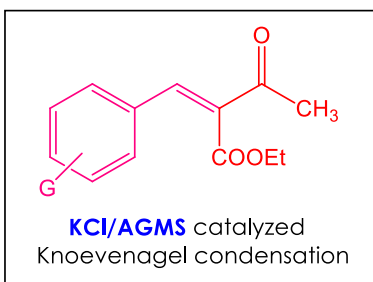
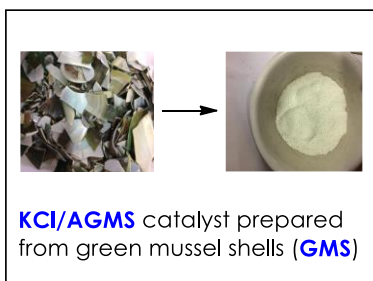
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Graphical abstract



Abstract

Knoevenagel condensation represents one of the most important C-C bond forming reactions in organic chemistry. The typical reaction was carried out commonly in the presence of homogeneous acid as well as basic catalysts. With the problems like corrosive and high catalyst amount, the search for a new heterogeneous catalyst is an attractive research topic in this area. KCl supported on activated green mussel shell (KCl/AGMS) was prepared by impregnation method and characterized by some analytical instrumentations (IR, XRD, SEM, EDAX). The prepared materials shows an incredible catalytic ability in Knoevenagel condensation of ethyl acetoacetate with aromatic aldehydes to produce condensed products 3a-3d in medium to good yields (60-94%). The findings disclose a mild route for the synthesis of Knoevenagel products using a cost-effective and green catalyst.

Keywords: Green mussel shell, KCl/AGMS, solid catalyst, Knoevenagel condensation

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1.0 INTRODUCTION

Knoevenagel condensation is a reaction between aromatic aldehydes/ ketones with active methylene compounds containing electron-withdrawing group [1]. It is an important organic reaction involving the formation of C-C double bond [1, 2], and has been widely used for production of various fine chemicals and construction of heterocyclic system such as coumarins, indoles and pyranopyrazoles [3-7]. Recently, Knoevenagel condensation was also developed as a testing reaction to evaluate the

catalytic performance of novel solid acid and base catalysts [8-11].

In common, many Knoevenagel condensation were carried out in the presence of homogeneous catalysts such as aliphatic and cyclic amines, indium(III), and ionic liquids [12-16]. In despite of their appreciable catalytic performance, the uncomfot issues in relation with separation and recycling procedures of the catalysts can not deal the growing request on clean and sustainable catalysis today [17]. Furthermore, corrosivity and requirement of high stoichiometric amount of the catalysts make them difficult to be applied in industrial scale.

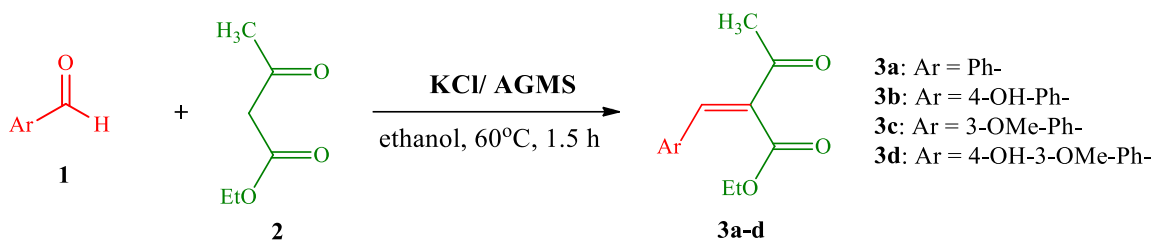


Figure 1 Reaction scheme of Knoevenagel condensation

Then, several studies have been focused on the utilization of solid base catalysts, such as g-C₃N₄ [18], Ca-containing mesoporous silica [19], hydroxyapatite supported cesium carbonate [20], methylated N-substituted SBA-15 [21] and Mg-doped graphitic carbon nitride [22]. Amine-grafted on lanthanide MOF [23] and amine-functionalized sugarcane bagasse [24] have also been employed. In addition, other solid catalysts like hydrotalcites [25], polymer microgel particles [26], and basic zeolites [27] were also well-to-do of catalyzing Knoevenagel condensation reaction. However, several of these methods have drawbacks like harmful reaction processes, low yield, toxic solvents, long reaction time and need of high reaction temperature. Thus, there is still a struggle for the development of mild protocols to carry out Knoevenagel condensation under green chemistry and simple work-up methods.

The material synthesized from the waste shells opens window for renewable catalyst and at the same time reutilize the waste generated. Previously, mussel shells have been explored for some purpose, such as catalyst in biodiesel synthesis [28], mercury removal [29] and effective biosorbent to absorb textile dyes from aqueous solution [30]. In this work, preparation and characterization of potassium chloride supported on activated green mussel shells (KCl/ AGMS) will be studied. Moreover, the catalytic capability of prepared material in Knoevenagel condensation will be noticed (Figure 1).

2.0 METHODOLOGY

2.1 General and Instrumentation

Ethyl acetoacetate and benzaldehyde derivatives were purchased from Merck and Sigma-Aldrich. Solvents and other chemicals were purchased from commercial suppliers. IR spectra were recorded on Shimadzu Prestige 21 FTIR spectrophotometer. SEM was performed with a SATW (CM-200, Phillips) tandem EDAX instrument. X-ray diffraction (XRD) patterns were recorded on a Phillips-1710 X-ray diffractometer with Cu-K α (0.154 nm) radiation in the range 2 theta degree of 0-90°. All reactions were monitored by thin layer chromatography (TLC) using silica coated on alumina plates. Mass analysis was

conducted on a Shimadzu QP Mass spectrometer 2010A with 70 eV electron ionization potential.

2.2 Preparation of KCl/AGMS Catalyst

Collected from household waste, empty natural green mussel shells (NGMS) were then washed with warm tap-water. The NGMS was washed with deionized water and dried at 120°C for 2 h. It was then grinded until get rough powders using an ordinary mortar and pestle. The GMS was calcined at 900°C for 4 h. The resulting material was denoted by activated green mussel shells (AGMS). Subsequently, KCl/AGMS catalyst was prepared using a wet impregnation method with modification of a reported work [31]. Typically, 5 g of AGMS was slowly immersed into 25 ml of aqueous solution containing 2.5 g of KCl with continuous stirring at room temperature for 3 h. The resulting white slurry was dried in an ordinary oven at 100°C for 2 h. Finally, the solid was calcined at 500°C for 3 h in air environment and this product was denoted as KCl/AGMS.

2.3 Procedure for Knoevenagel Condensation

To find the optimized conditions for Knoevenagel condensation, we explore the reaction between benzaldehyde and ethyl acetoacetate. Typically, benzaldehyde (2 mmol), ethyl acetoacetate (2 mmol) and ethanol (5 ml) were stirred in the presence of various catalyst amount. Temperature and reaction time were also varied. After completion (observed by thin layer chromatography with n-hexane: ethyl acetate 7:3 as eluent), hot ethanol was added into the reaction mixture. The mixture was filtered, and filtrate was evaporated under reduced pressure to give the solid product, (Z)-ethyl 2-benzylidene-3-oxobutanoate (3a). For the synthesis of Knoevenagel products using benzaldehyde derivatives, we used the optimized conditions obtained from model reaction.

2.3.1 Spectral Data of Compound 3a: (Z)-ethyl 2-benzylidene-3-oxobutanoate

Yellow solid; IR (KBr, cm⁻¹) 3050 (C-H sp² stretching), 3000-2970 (C-H sp³ stretching), 1660-1640 (C=O stretching), 1510 (C=C aromatic), 1450-1430 (C-H sp³ bending), 1226 (C-O stretching); MS (m/z) 218.0 (M⁺),

217.0 ($[M-1]^+$), 190.9, 173.0, 155.1, 131.0, 103.0, 77.1, 43.1.

2.3.2 Spectral Data of Compound 3b: (Z)-ethyl 2-(4-hydroxybenzylidene)-3-oxobutanoate

Yellow solid, IR (KBr, cm^{-1}) 3205 (O-H stretching), 3051-3020 (C-H sp^2 stretching), 2950-2880 (C-H sp^3 stretching), 1750 (C=O stretching), 1610 (C=C olefinic stretching), 1500-1480 (C=C aromatic), 1256 (C-O stretching); MS (m/z) 234.0 (M^+), 221.0, 209.9, 207.0, 190.9, 176.8, 162.9, 146.9, 120.9, 95.9, 73.0, 59.0, 44.0.

2.3.3 Spectral Data of Compound 3c: (Z)-ethyl 2-(3-methoxybenzylidene)-3-oxobutanoate

Yellow solid, IR (KBr, cm^{-1}) 3040-3000 (C-H sp^2 stretching), 2950-2800 (C-H sp^3 stretching), 1750 and 1720 (C=O stretching), 1605 (C=C olefinic stretching), 1501-1490 (C=C aromatic), 1220 (C-O stretching); MS (m/z) 248.1 (M^+), 217.0, 161.0, 102.0, 43.1.

2.3.4 Spectral Data of Compound 3d: (Z)-ethyl 2-(4-hydroxy-3-methoxybenzylidene)-3-oxobutanoate

Yellow solid, IR (KBr, cm^{-1}) 3400-3200 (O-H stretching), 3100-3000 (C-H sp^2 stretching), 2963-2820 (C-H sp^3 stretching), 1720-1700 (C=O stretching), 1612 (C=C olefinic stretching), 1503 (C=C aromatic), 1450-1400 (C-H sp^3 bending vibration), 1150 (C-O stretching); MS (m/z) 264.0 (M^+), 252.9, 206.9, 190.9, 155.9, 132.9, 96.0, 73.0, 44.0.

3.0 RESULT AND DISCUSSION

3.1 Characterization of KCl/AGMS

Nowadays, the utilization of waste materials as source of heterogeneous catalysts has been of interest in the development of sustainable catalytic processes [32]. Waste materials containing calcium carbonate are renewable [33], and they are often used as substrates to produce calcium oxide, a promising catalyst that are being used in various organic transformation [34-40]. Natural Green mussel shell (NGMS) was chosen as source of CaO because it mainly consists of calcium carbonate [28].

To analyze the functional groups, FT-IR spectrophotometry was applied in this work. NGMS in Figure 2(a) shows two major bands around 3600-3000 and 1485 cm^{-1} . The broad peak at 3600-3000 cm^{-1} is assigned to the stretching mode of O-H group in residual water molecule, while the band at 1485 cm^{-1} is associated with CO_3^{2-} stretching vibration in CaCO_3 . To confirm the functional groups on GMS and AGMS, we collected the FT-IR spectra and compared them. After thermal treatment, there is the detection of the 3650 cm^{-1} sharp band attributable to hydroxyl group due to surface interaction of water molecule with AGMS sample. Broadband around

600-400 cm^{-1} indicating the presence of Ca-O stretching vibration [36]. These peaks appeared after NGMS was calcined at 900°C. Identical FT-IR spectra between AGMS and KCl/AGMS indicating the same chemical functionalities in both samples.

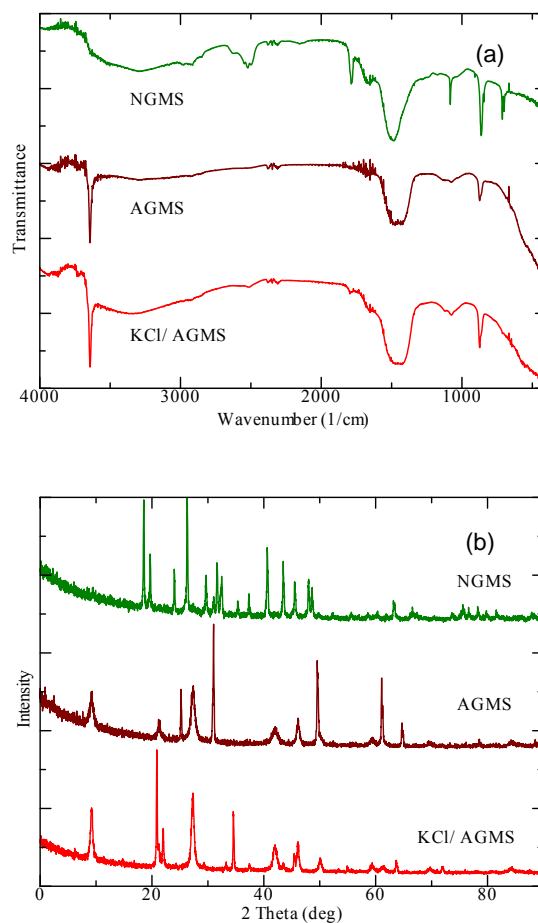


Figure 2 (a) FTIR and (b) XRD spectra of catalyst derived from natural green mussel shells (NGMS)

CaCO_3 content in NGMS was in the range of 95-99 % [41]. XRD results in Figure 2(b) reveal the composition of NGMS mainly consists of CaCO_3 in the form of vaterite phase, as indicated by strong diffraction peaks at 2θ of 24.6 and 27.0° [42-44]. The AGMS displayed peaks indicating the presence of CaO (2θ at 32.2°) and $\text{Ca}(\text{OH})_2$ (2θ at 28.7 and 34.1°) phases [45]. After impregnation with KCl and re-calcination at 500°C for 3 h, peaks corresponding to KCaCl_3 (2θ at 28.4°) and $\text{Ca}(\text{OH})_2$ (2θ at 34.1°) were produced, associated with small CaO peaks in KCl/AGMS catalyst [31].

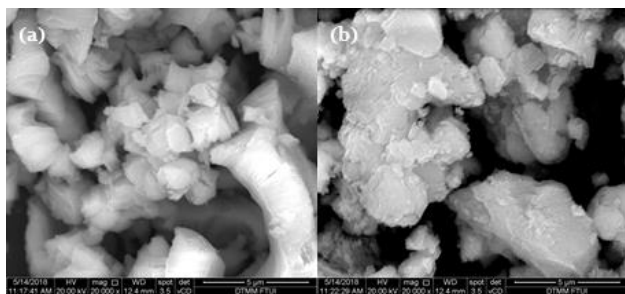


Figure 3 SEM images of (a) AGMS and (b) KCl/AGMS

The microstructure of AGMS and KCl/AGMS is shown in Figure 3. As investigated before, a typical layered architecture is the characteristic for mussel shells [46]. With calcination temperature at 900°C, the morphology changed to porous structure. The morphology conforms to those reported by Buasri *et al.* [28] and Hu *et al.* [47]. The AGMS shape was irregular, and some of them attracted together to form aggregates. After potassium chloride impregnation, the KCl/AGMS catalyst possess porous structure with large grains. KCl particles were observed in the surface of AGMS. Since AGMS and KCl/AGMS materials are less-porous, the particle size should directly correspond to surface area [28].

The elemental compositions of the AGMS and KCl/AGMS catalyst were studied by energy dispersive X-ray spectroscopy (EDS). It confirms that the AGMS was composed of Ca, O and C (Figure 4a). The amounts of Ca and O in the AGMS are found to be 35.36 and 58.71 wt%, respectively. Existence of C in EDS spectrum may due to the presence of uncalcined calcium carbonate in the AGMS sample. The EDS analysis of the KCl/AGMS indicated that the K and Cl content are 16.78 and 15.37 wt%. The result revealed the successive impregnation process.

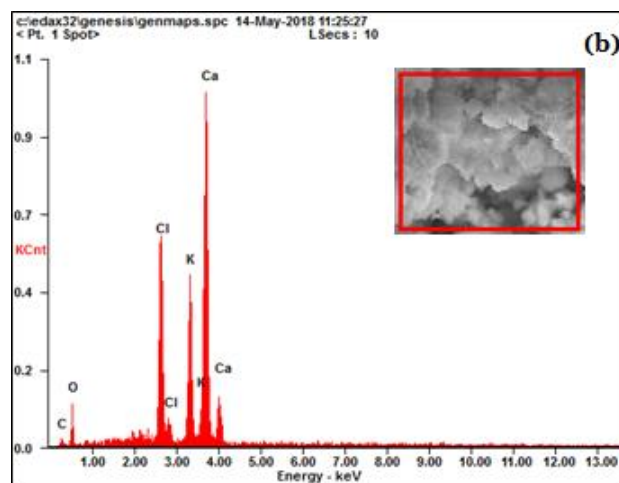
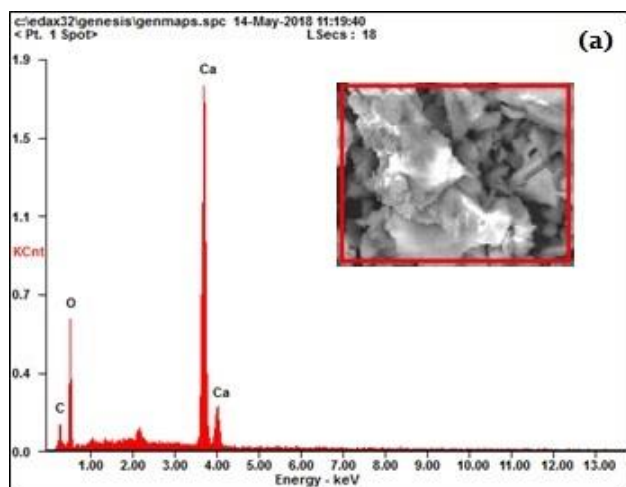


Figure 4 EDS spectra of (a) AGMS and (b) KCl/AGMS

3.2 Knoevenagel Condensation

Knoevenagel condensation has been considered as one of the most important reactions for producing carbonyl compounds integrated with C=C double bond and generally contains aromatic functionalities [48]. In this work, we explored the ability of KCl/AGMS for Knoevenagel condensation reaction between ethyl acetoacetate and benzaldehyde derivatives. For initial investigation of optimized conditions, benzaldehyde and ethyl acetoacetate are used as model substrates.

A series of experiments were conducted for 1.5h at room temperature and at 60°C in the absence of catalyst, which yields of product were isolated in trace (Table 1 Entry 1 and 2). The use of AGMS catalyst at room temperature and 1.5 h in the reaction generating 60% yield only (Table 1 Entry 6). The reaction furnished the highest yield up to 94% in the presence of 15 wt% of KCl/AGMS at 60°C for 1.5h (Table 1 Entry 7). The use of 20 wt% of catalyst under same conditions only give 86% yield (Table 1 Entry 8). To further verify the influence of temperature, the reaction was carried out at three different temperature. The increase of temperature up to 80°C did not affect any increase of product yield (Table 1 Entry 9).

Table 1 Optimization in Knoevenagel condensation using KCl/AGMS heterogeneous catalyst

Entry	Catalyst (wt%)	T (°C)	Time (h)	Yield ^b (%)
1	-	60	1.5	Trace
2	-	Rt	1.5	Trace
3	5	60	1.5	20
4	10	60	1.5	57
5	15	Rt	3	80
6	15 ^a	Rt	1.5	60
7	15	60	1.5	94
8	20	60	1.5	86
9	20	80	1.5	88

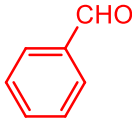
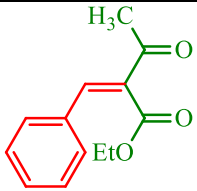
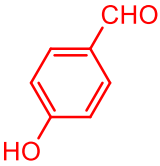
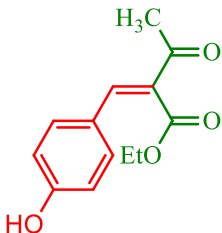
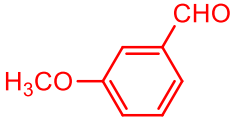
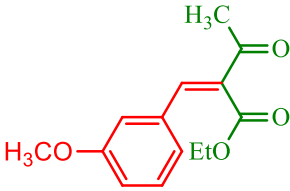
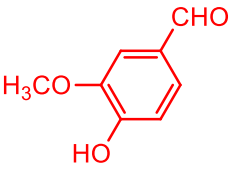
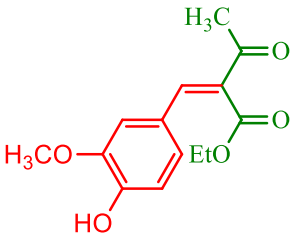
Reaction conditions: ethyl acetoacetate (2 mmol), benzaldehydes (2 mmol)

^a using AGMS catalyst

^b Isolated yield

Encouraged by the aforementioned results, Knoevenagel condensation of some aromatic aldehydes with ethyl acetoacetate catalyzed by KCl/AGMS in ethanol have been explored. As can be seen in Table 2, all products were obtained in good yields. The IR data of condensation products showed peak around 1610-1620 cm^{-1} indicating the existence of C=C olefinic group. Broad absorption band in the range of 3000-3600 cm^{-1} is found in the IR spectra of compound 3a, 3b and 3d, which corresponds to the presence of hydroxyl group. Meanwhile, in IR spectrum data of compound 3c, there is no peak for OH group. The peak for sp^3 C-H and C=C stretching can clearly be seen. Mass spectra measurements were done to elucidate the condensation products with specific molecular cation peaks in their spectra.

Table 2 Knoevenagel condensation of benzaldehyde derivatives

Entry	Aldehyde	Product	Yield (%)
3a			94
3b			60
3c			73
3d			85

Reaction conditions: KCl/AGMS catalyst 15 wt%, at 60°C, 1.5h reaction time, in ethanol.

The proposed mechanism of Knoevenagel condensation is stated below (Figure 5). KCl/AGMS is CaO-based material and considered as base catalyst. The catalyst will deprotonate methylene group of ethyl acetoacetate to give enolate ion. Then it will undergo nucleophilic addition with benzaldehyde. After protonation, a typical β -hydroxy

carbonyl is obtained. In the final step, dehydration of this intermediate will give Knoevenagel product.

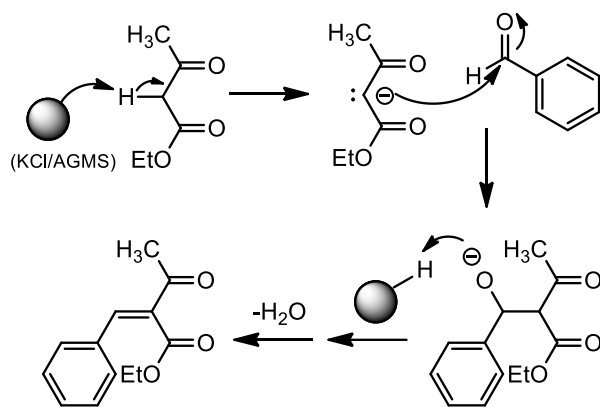


Figure 5 Proposed mechanism of this Knoevenagel condensation

4.0 CONCLUSION

In conclusion, KCl/AGMS solid base catalyst has been successfully prepared from green mussel shells waste by thermal activation then wet impregnation method. The impregnated KCl into AGMS was confirmed by EDAX spectroscopy. We have established a simple catalyst for C-C bond construction via Knoevenagel condensation reaction having high activity to generate products in good yields.

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