

Ca@Al-BENTONITE: A NEW MATERIAL FOR CHALCONE PRODUCTION

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ABSTRACT

Solid catalyst of Ca@Al-Bentonite was prepared by modifying natural bentonite which collected from Bogor, Indonesia via pillarization of Al and wet impregnation of Ca particles. The catalyst was characterized by means of FTIR, XRD, XRF and BET surface area. The catalyst is successful to use for Aldol condensation in chalcone synthesis.

Keywords: bentonite, Ca@Al-Bentonite, chalcone, Aldol condensation, solid catalyst.

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INTRODUCTION

Chalcones, which structurally corresponds to *trans*-1,3-diaryl-2-propen-1-ones, represent an attractive class of natural products that are found abundantly in higher plants including vegetables and fruits.¹⁻⁵ They denoted remarkable biological advantages such as anticancer, anti-inflammatory, antioxidant, antimalarial, antitubercular and antimicrobial activities.⁶⁻¹¹ Generally, chalcones are produced by using base catalysts via Claisen-Schmidt Aldol condensation.¹²⁻¹⁴ Indeed, due to the interesting application of chalcones, many novel synthetic methodologies have been utilized.¹⁵⁻¹⁷

In the modern era of chemical technology, a change in emphasis towards more environment-friendly chemical synthesis has become a major challenge.¹⁸ Green Chemistry, or Sustainable Chemistry, is formulation and design of products and processes that minimize or remove the use or generation of hazardous materials.^{19,20} The example of realization of Green Chemistry principles is in the field of organic transformation which is carried out in mild condition by using heterogeneous catalysts, as they safer to the environment and have unique properties. One of the promising material for catalysis purpose is bentonite clay.²¹ It has been widely used as a catalyst for hydrogenation of nitrobenzene to aniline²², transesterification in biodiesel production²³, cyclohexene epoxidation²⁴ and partial hydrogenation of benzene to cyclohexene²⁵. In this work, we prepared Ca@Al-Bentonite, a new kind of modified bentonite, for chalcone production.

EXPERIMENTAL

Materials

Natural bentonite was collected from Bogor, Indonesia. All chemicals were analytical grade and used without further purification. Infrared spectra were recorded on Shimadzu Prestige-21 FTIR spectrophotometer. XRD measurements were conducted on Rigaku MiniFlex 600 X-Ray Diffractometer. The chemical composition of bentonite was determined using X-Ray Fluorescence PANalytical Epsilon 1. The surface area of modified bentonite was measured using BET method. Chalcone structure was confirmed by LC-MS instrument.

Preparation of Natural Bentonite

Natural bentonite (200 g) was ground to a fine powder using mortar, then dried in the oven at 110°C for 2h and filtered by using 200 mesh of a molecular sieve. The fine powder was dissolved in 2M of acetic acid. The mixture was stirred and refluxed at 80°C for 4-6 h. The precipitate was separated and washed three times using deionized water. Finally, the precipitate was dried in an oven at 120°C for 24 h and stored in a desiccator. Cation exchange capacity of natural bentonite was measured using previously reported

method.²⁶ Powder of natural bentonite was analyzed by FTIR, XRD, XRF, and BET surface area. After analysis, powder of natural bentonite was found as Ca-bentonite.

Preparation of Al-Bentonite and Ca@Al-Bentonite

Al-Bentonite was prepared by the following procedure. First, a solution of polycation Al was made by adding 495 ml of NaOH (0.2M) into 450 ml of AlCl₃ (0.1M) until the ratio of hydroxide:Al was 2.2:1. The mixture was stirred and then aged for 48h. Pillarization was done by mixing and stirring 945 ml of polycation Al with activated natural bentonite (2% suspension in water) at room temperature. The mixture was centrifuged and then the precipitate was washed with deionized water. The solid was tested using AgNO₃ solution to check the absence of chloride ion in the sample. Then, dried at 40°C for 72h and calcined at 400-600°C for 3.5 h. This sample is denoted as Al-Bentonite.

Ca@Al-Bentonite was prepared by wet impregnation method of Ca²⁺ (from CaCl₂) into Al-Bentonite. A sample of Al-Bentonite (10 g) was weighed and added to calcium chloride solution until the final concentration of Ca²⁺ is 20% per total mass of Al-Bentonite. The mixture was stirred for 4-6 h at 40-60°C. The solid was collected, washed and checked until negative test with an AgNO₃ solution. Finally, the solid was dried at 80-100°C and calcined at 400°C for 4 h. The solid obtained is indicates as Ca@Al-Bentonite.

Synthesis of Chalcone

In a round-bottom flask, 2-hydroxyacetophenone (2 mmol), benzaldehyde (2 mmol), ethanol (5 ml) and Ca@Al-Bentonite (10% wt.) were refluxed at 70°C for 4 h. The product was separated from the reaction mixture by filtering to give a clear solution. The solution was concentrated at room temperature to yield yellow solid. The solid obtained then recrystallized in hot ethanol to produce yellowish crystals and analyzed by LC-MS.

RESULT AND DISCUSSION

The XRD pattern of natural bentonite is shown in Fig.-1 and it has peak at 2θ of 5.6693° with basal spacing 15.5712 Å which indicates the type of bentonite in the sample is calcium-based bentonite. This data was supported by Zhang *et al.* in their previous work.²⁷ The result of XRF analysis is in line with the XRD result, with Ca content of 2.615% (Table 1). Cation exchange capacity of natural bentonite was determined using methylene blue and found to be 35.84 meq/100 g.

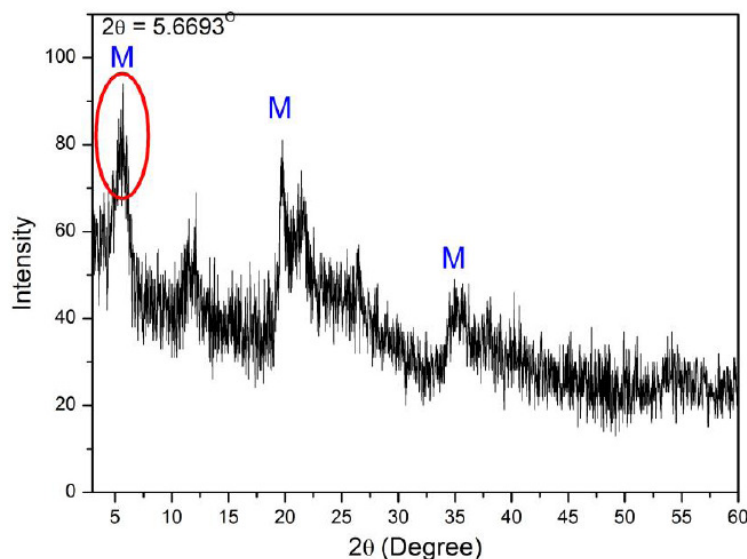


Fig.-1: XRD pattern of natural bentonite

Table-1: Chemical Composition of Natural Bentonite

Composition	Si	Al	Fe	Ca	Mg	K	Cl	Ti
Wt. %	42.076	15.149	29.623	2.615	6.340	1.214	1.009	1.974

The typical FTIR curves were recorded and the result shows in Fig.-2. The absorption band in the area of 3620 cm^{-1} is observed that is characterized by OH stretching vibration of Al(Mg)-O-H. The band at 1638 cm^{-1} also associated to OH deformation of H_2O molecules. The Si-O-Si vibration of tetrahedral bentonite sheet is observed at 1103 and 1041 cm^{-1} region. The peak at 522 cm^{-1} is characteristic for Si-O-Al bending vibration. Meanwhile, the bending vibration of OH group is observed at 913 cm^{-1} . The peak at 3620 cm^{-1} shifted to a lower intensity as the bentonite is calcined and modified with Al and Ca. The FTIR patterns of activated natural bentonite, Al-bentonite and Ca@Al-Bentonite are very identical that indicates these material is having a similar chemical compositions.

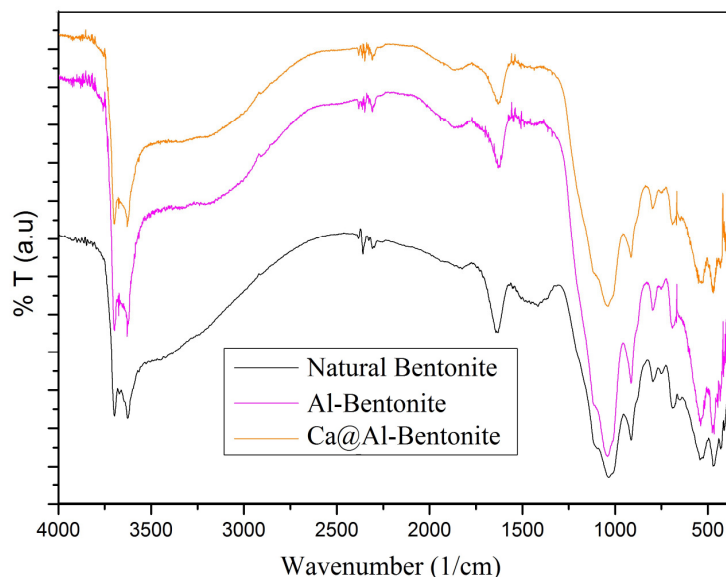


Fig.-2: FTIR spectra of natural and modified bentonite

XRD patterns of the natural and modified bentonite are shown in Fig.-3. Characteristics of each bentonite sample can be shown in the 2θ region of $2-7^\circ$. Natural bentonite, Al-Bentonite and Ca@Al-Bentonite have a different peak at 5.63° , 4.65° and 4.87° , respectively (Table 2). Based on the XRD analysis, the basal spacing of natural bentonite was 15.69 \AA , while the spacing of Al-Bentonite and Ca@Al-Bentonite were enlarged to 18.97 and 18.15 \AA , respectively. It is caused by the intercalation of Al and Ca particles in the interlayers of bentonite.

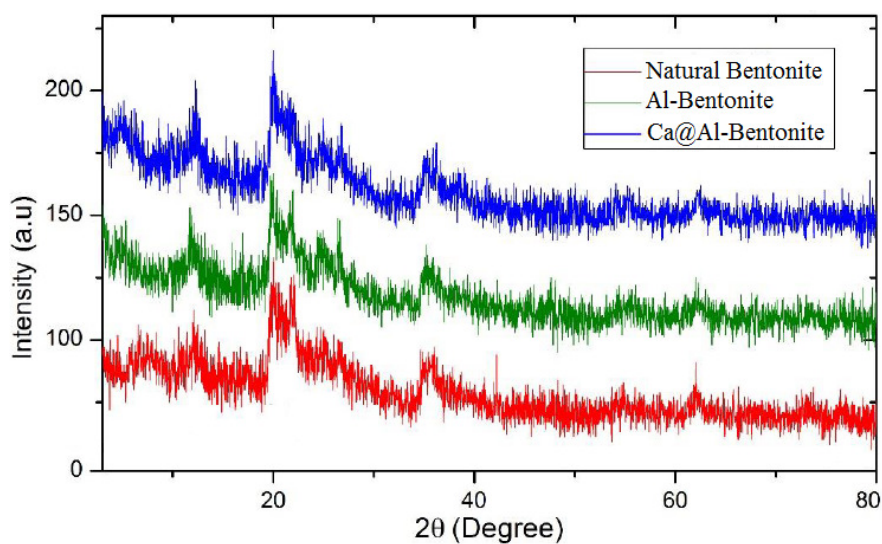


Fig.-3: XRD spectra of natural and modified bentonite

Table-2: Basal spacing values at specific 2θ

Sample	2θ (degree)	d_{001} (Å)
Natural Bentonite	5.63	15.69
Al-Bentonite	4.65	18.97
Ca@Al-Bentonite	4.87	18.15

The BET surface areas, average pore radius, and pore volume of the prepared materials are summarized in Table 3. A specific surface area of 62.75 m²/g was observed for the natural bentonite. After modification with Al and Ca particles, the surface area and average pore volume of modified bentonite are increased significantly. This may indicate the successive Al pillarization and Ca impregnation to the natural bentonite. The increase of surface area may be attributed to the incorporation of Ca²⁺ not only in the interlayer, but also on the external surface of bentonite.

Table-3: Result of characterization using BET

Sample	Surface Area (m ² /g)	Average Pore Radius (nm)	Average Pore Volume (cc/g)
Natural Bentonite	62.75	4.14	0.13
Al-Bentonite	80.18	3.99	0.16
Ca@Al-Bentonite	103.89	3.60	0.19

The nitrogen adsorption isotherms of natural bentonite, Al-bentonite and Ca@Al-Bentonite are identical for all the samples. The profile of Ca@Al-Bentonite exhibited the typical type II isotherm (Fig.-4).

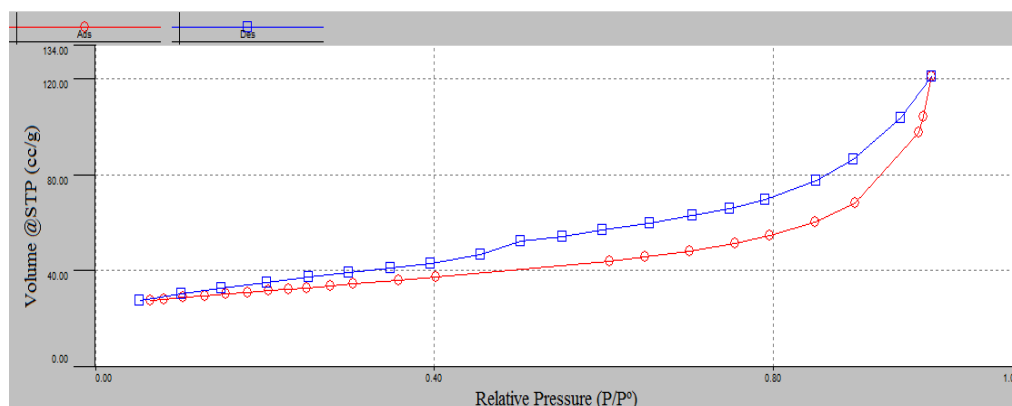
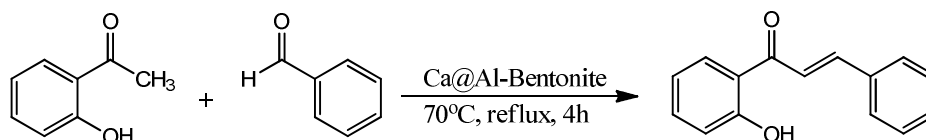


Fig.-4: Adsorption and desorption profile of Ca@Al-Bentonite

The Ca@Al-Bentonite then was applied as a solid acid catalyst in chalcone production. For model compound, 2-hydroxyacetophenone and benzaldehyde were chosen as starting material to give corresponding chalcone, (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one. The LC chromatogram was depicted in Fig.-5, the product has a retention time of 17.37 min, and based on evaluation using MS instrument, the sample has *m/z* of 225. The isolated yield of pure chalcone was found to be 65%.

In the first step, the acidic catalyst interacts with the oxygen atom in carbonyl group of benzaldehyde. It will activate carbonyl group and make the compound easier to react via nucleophilic addition. On the other hand, 2-hydroxyacetophenone will change to enol form in an equilibrium system. An electron in the C-C double bond of ketone will attack the activated carbonyl group of benzaldehyde to give β -hydroxychalcone. It was subsequently dehydrated to give chalcone compound.



Scheme-1: Production of chalcone using Ca@Al-Bentonite

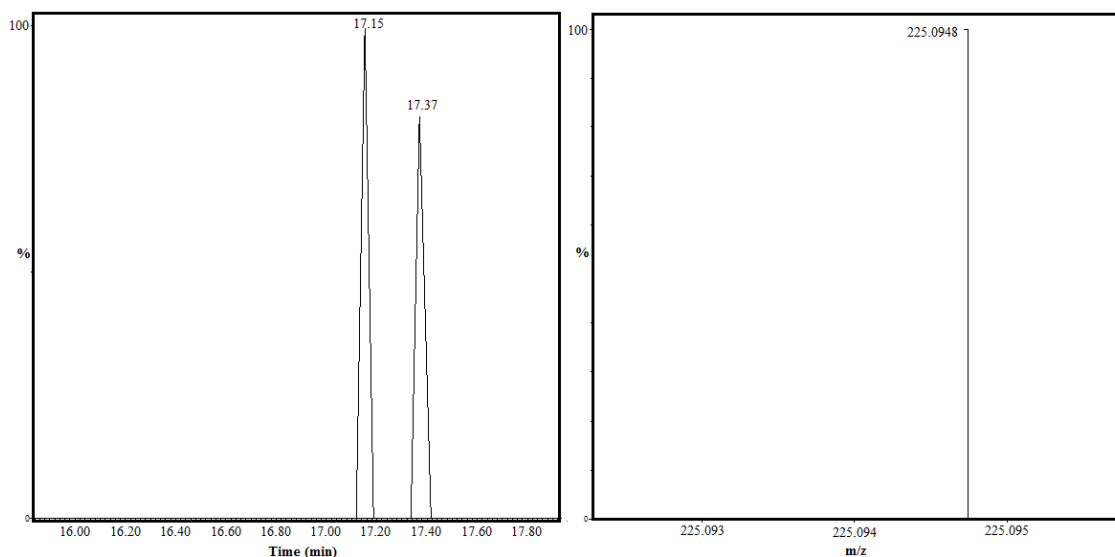


Fig.-5: LC profile of chalcone

CONCLUSION

Ca@Al-Bentonite is successfully prepared by wet impregnation method of Ca^{2+} into Al-Bentonite. It has the largest surface area compared to Al-bentonite and natural bentonite. In catalysis application, the Ca@Al-Bentonite material shows promising activity in the chalcone production from the reaction of 2-hydroxyacetophenone and benzaldehyde as a model compound.

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