Chemistry International 1(4) (2015) 196-201

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Catalytic acetylation of (+)-cedrol with heterogeneous catalyst H_2SO_4/SiO_2 under solvent free conditions

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A R T I C L E I N F O

Article type:
Research article
Article history:
Received May 2015
Accepted June 2015
October 2015 Issue
Keywords:
Heterogeneous catalyst
H_2SO_4/SiO_2
Acetylation
(+)-cedrol

A B S T R A C T

Heterogeneous catalyst, H_2SO_4/SiO_2 was synthesized by immobilizing sulfuric acid on silica gel as solid support. Silica gel was prepared from kaolin, originating from Belitung island Indonesia. The synthesized catalyst was characterized by various techniques such as X-Ray diffraction, Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy and BET method and was applied for the acetylation of (+)-cedrol compound using acetic anhydride under solvent free conditions. The optimum conditions for catalytic acetylation were found at 353 K for 20 h reaction period, the molar ratio (+)-cedrol/acetic anhydride 1:10 in the presence of 5%-w of catalyst converted 88,7% (+)-cedrol into cedryl acetate. Results revealed catalyst could possibly used cedryl acetate synthesis from (+)-cedrol.

Capsule Summary: Heterogeneous catalyst, H_2SO_4/SiO_2 from kaolin was successfully used for acetylation of (+)-cedrol with significantly higher yield.

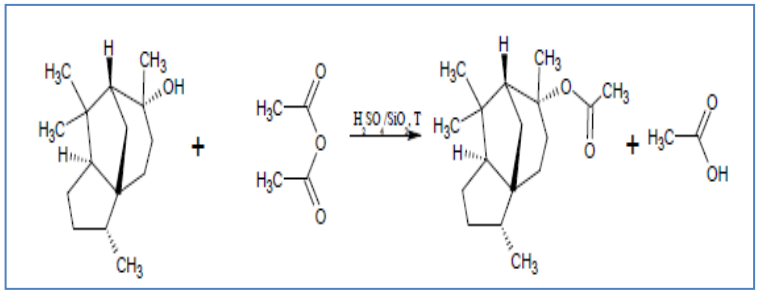
Cite This Article As: Elvia, R., Cahyana, A.H., Wibowo, W. 2015. Catalytic acetylation of (+)-cedrol with heterogeneous catalyst H_2SO_4/SiO_2 under solvent free conditions. Chemistry International 1(4) (2015) 196-201

INTRODUCTION

Kaolin has been identified as a potential raw material for the production of γ-Al_2O_3 for multi purpose catalyst support. High-quality kaolin from Belitung island, Indonesia is used as a mixture of domestic soap and cosmetics, while the low-quality kaolin functioned as an ingredient for making ceramics. Kaolin is one of the several types of clay minerals, and correctly known as kaolinite with the chemical composition $Al_2Si_2O_5(OH)_4$. This hydrated silica alumina contains approximately of 46% SiO_2, 40% Al_2O_3, and 14% H_2O. Thus, it can be used as silica source for the preparation of silica gel. Silica gel is an amorphous and porous solids formed by the polymerization of silicic acid, is neutral, inert and has a great adsorption capacity, so that silica gel is usually used as catalyst support.

The heterogeneous catalysts for organic synthesis have been intensively applied in the recent decades due to their unique physical and chemical properties such as shape, selectivity, acidic and basic nature and their thermal stability. The advantages of these catalyst systems over homogeneous systems are well known, such as stability, ease of handling, lack of corrosion and other environmental hazards, ease of recovery and regeneration (Subhan et al., 2001).

(+)-Cedrol is a sesquiterpene natural product isolated from cedarwood oil extracts of *Juniper* species trees. Cedrol compound and its derivatives have efficacy as sedative, pain reliever and irritation of the respiratory tract ,thus the transformation of functional groups cedrol compounds are needed to produce derivatives with the desired aroma effect such as cedryl acetate. Cedrol is fragrance ingredients used in decorative cosmetics, fine fragrances, shampoos, toilet soaps and other toiletries as well as in non-cosmetic products such as



Scheme 1: Acetylation of (+)-cedrol compound

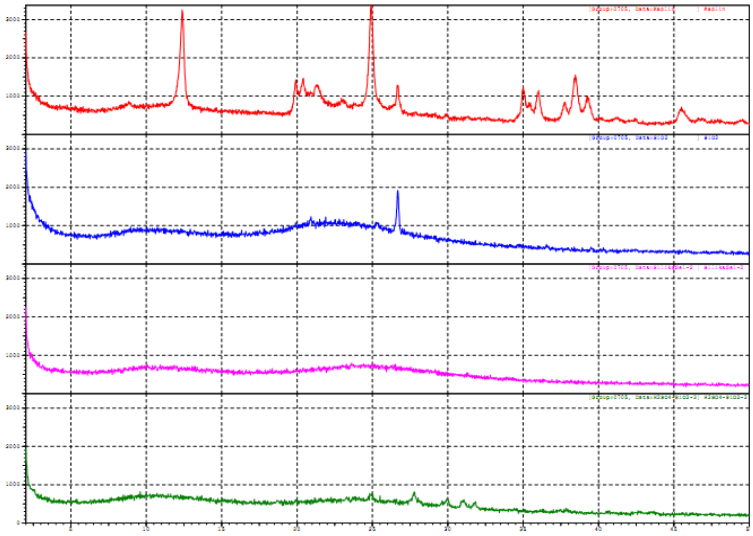


Fig. 1: Diffractogram, (a) kaolin, (b) obtained silica (SiO_2), (c) Silica Gel, (d) H_2SO_4/SiO_2

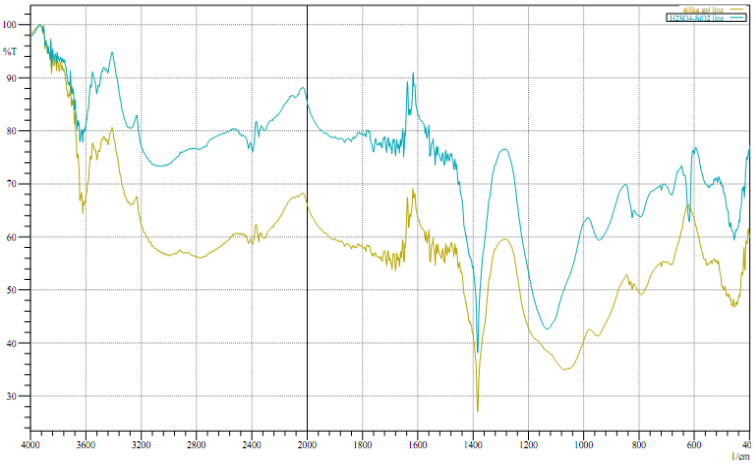


Fig. 2: FTIR spectra of, (a) silica gel, (b) H_2SO_4/SiO_2

household cleaners, and detergents (Bhatia et al., 2008). Cedrol can be converted to cedryl acetate by acetylation.

Acetylation of alcohols is an important and routinely utilized transformation in organic chemistry (Subhan et al., 2001). Specifically, acetylation refers to that process of introducing an acetyl group into a compound, namely, the substitution of an acetyl group for an active hydrogen atom. A reaction involving the replacement of the hydrogen atom of a hydroxyl group with an acetyl group (CH_3CO) yields a specific ester, the acetate. The most notable of acetic anhydride is for the acetylation of alcohols used reagent combination for this reaction in the presence of acid or base catalysts (Pearson et al., 1999). Tertiary alcohols have been esterified in good yields using acetic anhydride with calcium hydride or calcium carbide, t-butanol can be esterified to t-butyl acetate in 80% yield under these conditions (Pearson et al., 1999). Various catalyst such as zeolite H-FER (Subhan et.al., 2001), $Zr(HSO_4)_4$ (Chakraborti et al, 2009), silver triflate (Das et al., 2011), silica sulfuric acid (Shirini et al., 2005), lithium (bisfluorosulfonyl)-imide (Li et al., 2012), iodine (Phukan, 2004) and heteropolyacid (Heravi et al., 2007) have also been used for the acetylation of alcohols. Most of these reported catalyst used Ac_2O as acetylating agent.

Herein we report the acetylation of (+)cedrol compound by using acetic anhydride in the presence of a catalytic amount of H_2SO_4/SiO_2 under solvent free conditions (Scheme 1). Silica sulfuric acid as an efficient and reusable heterogeneous catalyst was used for the preparation of 2H-indazolo[2,1-b]phtalazine-triones (Shaterian et al., 2008) and it was efficient reagent for the acetylation of alcohols in solution and under solvent free conditions (Shirini et al., 2004).

MATERIALS AND METHODS

Materials

Mineral kaolin, used as the silica sources in the synthesis of catalyst H_2SO_4/SiO_2, is a commercial grade product in fine powder produced by PT Kaolindo Sakti Perkasa, Belitung, Indonesia. Other chemicals employed were HNO_3 65%, H_2SO_4 95%, HCl 37%, K_2CO_3 p.a , diethyl ether for analysis from Merck and demineralized water. The chemicals used in the catalytic reaction were cedrol and acetic anhydride 97% from Ajax.

General Procedure for catalyst synthesis

Kaolin was first calcined at 800^0C for 6-h to obtain meta-kaolin. X-Ray Diffraction analysis were conducted to observe the transformation of kaolin to meta-kaolin. For extraction of SiO_2 from meta-kaolin as solid support in this catalyst, meta-kaolin was refluxed by aquaregia (mixed of HNO_3 and HCl) with stirred magnetically at 100^0C. The precipitate was filtered and washed with demineralized water until the pH of the washing water was 7, and then it was dried at 110^0C. The results from steps above is SiO_2 powder. For the preparation of silica gel, silica powder mixed with Na_2CO_3 with mole ratio 1 : 1 and the mixture crushed until smooth and homogeneous, then it was heated at 800^0C. After 24 h, it was immersed in demineralized water for 12 h and filtrate was filtered. Filtrate was added with a dropwise HNO_3 6

Table 1: Chemical compositions of kaolin

Element	Norm C, wt.%
Oxygen	64.25
Pottasium	0.32
Silicone	15.61
Indium	0.56
Sulfur	0.04
Alumunium	18.56
Iron	0.66

Table 2: Acetylation of (+)cedrol under different conditions

Run	Temperature	H_2SO_4/SiO_2	Time	Yield
	K	% w/w	h	%
1	353	Nil	20	59.66
2	353	5	10	57.57
3	353	5	15	77.7
4	353	5	20	88.69
5	353	10	20	77.78
6	363	5	5	18,00
7	363	5	10	46.09
8	363	5	15	51
9	363	5	20	50.36
10	363	5	25	41.47

M to formed silica hydrosol, then it was kept at room temperature for 48 h for polymerization to silica gel. It was filtered and washed with demineralized water, and dried at 110^0C. For the preparation of H_2SO_4/SiO_2 catalyst, to a suspension of silica gel in Et_2O (5 mL ether per gram silica gel) was impregnated of H_2SO_4, and the mixture was stirred magnetically at room temperature. The Et_2O was removed under reduced pressure and the residue heated at 100^0C for 72 h.

Characterization of the Synthesized Catalyst

X-Ray Diffraction, FTIR Spectroscopy, Surface area Analysis and SEM measurements were employed to characterize the synthesized catalyst. The specific surface area was determinated by using BET methods by Quantachrome NOVA Win1000. Mineralogical analyses and the crystallinity of the synthesized catalyst were performed by X-ray Diffraction (XRD) on a Shimadzu X-Ray Diffractometer 7000 using Cu K_α radiation and a Ni filter. The scanning range of 2θ was set between 2^0 and 50^0. FTIR spectra of kaolin, silica gel and catalyst were recorded using Shimadzu IRPrestige-21, Fourier transform infrared spectrophotometer. Transmission mode was employed by using the powder technique with KBr pellet. The morphology of the synthesized catalyst was determined by Scanning Electron Microscopy, Zeiss EVO 50.

Catalytic Acetylation and Analysis

The catalytic acetylation was carried out in a two necked-flask reactor equipped with a stirrer and a reflux condenser to ensure good mixing and prevent loss of volatile compounds. The reaction was performed at 353 K and 363 K under atmospheric pressure.

To a mixture of acetic anhydride (10 mmol) and cedrol (1 mmol), the catalyst (0.02 g, 5% w/w from cedrol)) was added and the reaction mixture were stirred at 353 K for the length of time, from 10 h up to 20 h. After the completion of the reaction, the reaction mixture was diluted with EtOAc and filtered to remove the catalyst. The filtrate was washed with NaOH 5% to remove another product and neutralized of exceed of acetic anhydride. The organic layer was then dried over anhydrous Na_2SO_4 and filtered. For a comparative study, catalytic acetylation of (+)cedrol was conducted with and without

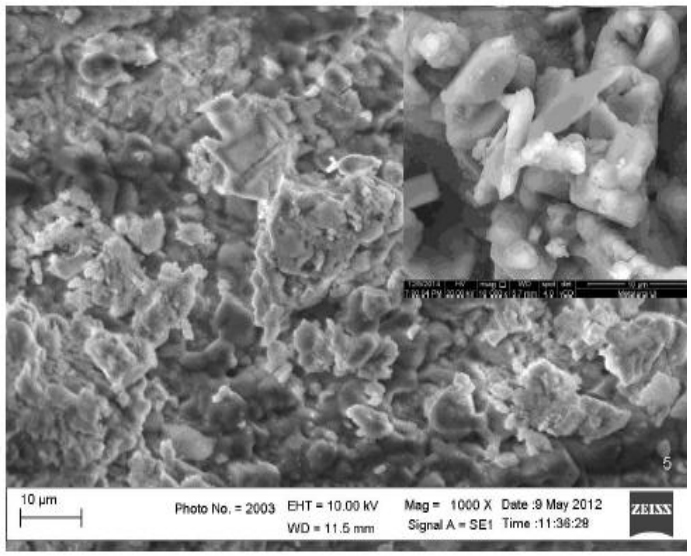


Fig. 3: Scanning electron micrographs of synthesized catalyst

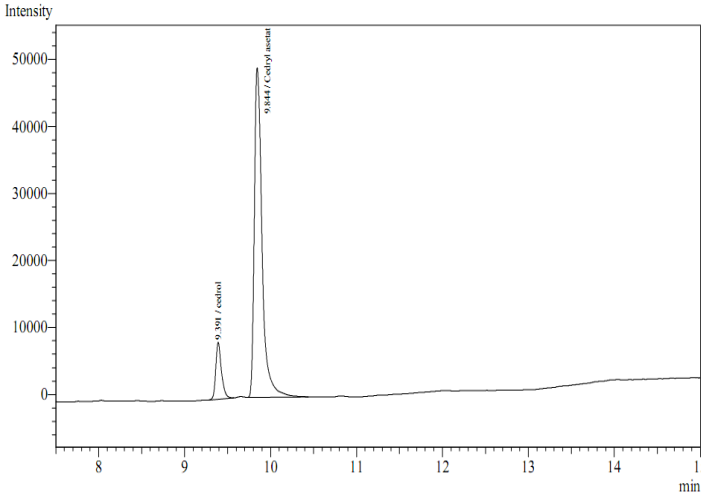


Fig. 4: Chromatogram of catalytic acetylation product

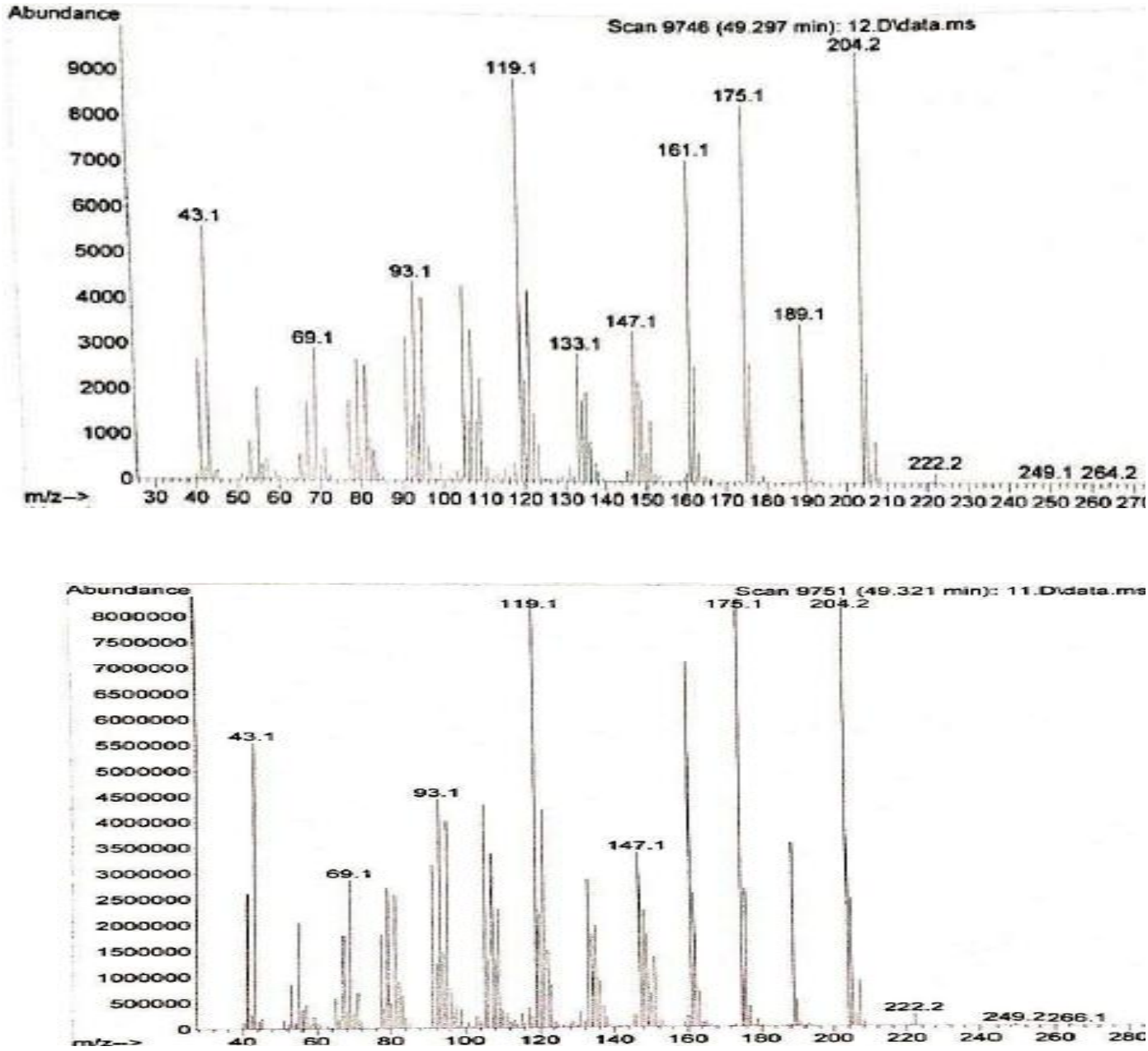


Fig. 5: Fragmentation of cedryl acetate by Mass Spectroscopy (upper) standard, (below) product acetylation

H_2SO_4/SiO_2 catalyst.

The reaction products were analyzed by Gas Chromatography Shimadzu 2010 (column : HP-20M, Carbowax), using (+)cedrol and cedryl acetate as standard references and by Gas Chromatography – Mass Spectrometric.

RESULTS AND DISCUSSION

Catalyst Synthesized and Characterization

The original kaolin contains mainly SiO_2, Al_2O_3, and some amount of Fe_2O_3. The elements constituent of kaolin sample used in the present study are given in table 1.

The heat treatment on kaolin transforms kaolin into metakaolin. Dehydration by thermal treatment converts kaolin to metakaolin, which is semicrystalline and much more reactive than the starting material (Akolekar et al., 1997).

$$Al_2Si_2O_5(OH)_4(\text{kaolin}) \xrightarrow{1073K} Al_2Si_2O_7(\text{metakaolin}) + 2H_2O$$

The XRD pattern of metakaolin show that kaolinit was transform into metakaolin and its pattern mainly represents the presence of SiO_2 quartz and pottasium aluminium silicate. SiO_2 quartz was extracted from metakaolin by reflux with aquaregia at 100^0C as white powder. And then, by polymerization of SiO_2, silica gel

was formed. The white gel obtained was amorphous in nature which can be used as catalyst support of sulfuric acid.

Figure 1. shows the diffractograms of the kaolin (a), obtained silica (SiO_2) (b), Silica gel (c) and H_2SO_4/silica gel (d). The XRD pattern of original kaolin mainly represents of kaolinite. Figure 1b and 1c shows that SiO_2 (quartz) was successfully extracted from metakaolin and silica gel was successfully formed from SiO_2 (quartz). On the other hand, XRD patterns in Figure 1(d) show that H_2SO_4/SiO_2 catalyst was formed.

The FTIR spectra of silica gel and H_2SO_4 /SiO_2 are shown in Figure 2 which consists of bands at 3615, 3140, 2393, 1687, 1382, 1130, 945, 795 and 619 cm^{-1}. The bands at 1687 and 3140 cm^{-1} are assigned to OH bending and stretching vibrations respectively. The band observed at 945 cm^{-1} is assignable to Si—O vibration modes of isolated Si—OH groups respectively (Waseem et al., 2009) . The peak at 795 cm^{-1} may be assigned to the O-Si-O vibration mode of SiO_2 and the peak at 1130 cm^{-1} is assignable to S=O stretching symmetric (Pavia et al., 2009) from impregnated of H_2SO_4 to silica gel. The band observed at 1380 cm^{-1} may be attributed to the presence of NO_3^- anions (Waseem et al., 2009) .

Figure 3. shows the micrograph of the synthesized catalyst, although the crystal morphology of the catalyst is not specific, because the synthesized catalyst has impurities with the presence of big cations especially is potassium. Surface area analysis with BET methods showed that H_2SO_4/SiO_2 catalyst had surface area of 1.345 m^2/g, total pore volum 1.23 x 10^{-2} cc/g and average pore radius 183 Å.

Catalytic Acetylation and Analysis

The synthesized catalyst H_2SO_4/SiO_2 was applied for the acetylation of (+)cedrol compound using acetic anhydride under solventless conditions. Products of acetylation was analyzed by Gas Chromatography and Mass Spectra, and the optimum conditions for catalytic acetylation was found at 353 K for 20 h reaction period, with molar ratio (+)cedrol/acetic anhydride 1:10 in the presence of 5%-w of catalyst in which 88,7% (+)cedrol was converted into 88,7% cedryl acetate (see table 2).

Figure 4 shows the chromatogram of acetylation product. It shows that, cedryl acetate was obtained successfully from (+)-cedrol after catalytic reaction with H_2SO_4/SiO_2 as heterogeneous catalyst and the meanwhile, fragmentation of cedryl acetate standard and the product acetylation were obtained by mass spectroscopy are shown in figure 5.

CONCLUSIONS

Synthesized catalyst H_2SO_4/SiO_2 was succesfully used as a acidic catalyst for acetylation of (+)cedrol compound by using acetic anhydride under solvent free conditions. Cedryl acetate was obtained in good yields under operationally simple experimental conditions.

ACKNOWLEDGEMENT

The Indonesian Ministry of Education and Culture for postgraduate scholarship and Prof. Ha Won Kim from University of Seoul for the sample.

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