

Research Article

ZnO–Porous Clay Heterostructure from Saponite as Green Catalyst for Citronellal Cyclization

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Abstract

Green conversion in organic synthesis is one of the interesting and important topics in green chemistry. The use of heterogeneous catalysis instead of homogeneous catalysis offers some advantages, such as easy separation and reusability. In this research, a heterogeneous acid catalyst was prepared from saponite by immobilizing ZnO in the form of a pillared clay (Zn/PILS) and Zn supported on porous clay heterostructure (Zn/PCH). Physicochemical studies involving X-ray diffraction measurement, surface analysis using a gas sorption analyzer, and surface acidity measurement were performed. Results indicated that the increasing surface acidity and the high specific surface area of the material were the relevant physicochemical properties that facilitate environment-friendly citronellal cyclization. The higher values for both parameters in Zn/PCH than in Zn/PILS linearly affected citronellal conversion and the selectivity for isopulegol production. Zn/PCH demonstrated a conversion rate of 98.9% for a 3-hour reaction and a selectivity of 100% for isopulegol production, and it exhibited reusability properties. Copyright © 2020 BCREC Group. All rights reserved

Keywords: Citronellal; Cyclization; Pillared Clay; Porous Clay Heterostructure; ZnO

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1. Introduction

Citronellal is a component of lemon grass oil and is an important compound for several platforms used to produce some pharmaceuticals and toiletries. Citronellal can be converted into isopulegol through several mechanisms, one of which is isomerization over an acid catalyst [1]. This step is important given that other compounds, such as menthol, can be derived from isopulegol. The catalytic approach in the conversion of citronellal into isopulegol has been wide-

ly studied. From the green chemistry perspective, the use of a heterogeneous catalyst instead of a homogeneous catalyst for such conversion has been considered, and the use of some alternative catalysts has been reported. Besides the economic value of catalysts, their high surface area, acidity, and stability are important properties to consider [2]. The formation of metal oxide pillared clays in some catalytic applications, including citronellal cyclization, was widely reported [3-5]. The preservation of surface Brønsted and Lewis acidities plays an important role in an effective and recyclable catalytic mechanism. In silica-alumina materials, clay-based catalysts exhibit a high surface area,

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and they are modifiable and reusable. Some modification schemes can be applied to identify more active catalysts for the homogeneous distribution of a metal or a metal oxide catalyst in a clay structure. Studies showed that the formation of metal oxide in the interlayer space of smectite clay structures provides stability and more importantly preserves the surface acidity in certain acid-catalyzed mechanisms [6-8]. Modification of a clay into a porous clay heterostructure (PCH) was also reported. PCH attracts considerable interest for catalysis applications and has been reported in various reactions, including DeNO_x process, dehydration, and photodegradation [6,7,9,10].

High surface acidity and high surface area are the main factors influencing the increase in catalytic activity; moreover, the advantages of using PCH especially in preserving surface acidity in many catalytic mechanisms are mainly attributed to the tunable properties of PCH. The combination of acid metal oxide and PCH was also notified to give mutual properties for some desirable properties in reactions, including the catalyst activity and selectivity refer to the presence of metal as active site specificity [11-13].

In industrial applications, citronellal conversion requires the use of a reusable, efficient, and effective acid catalyst instead of a non-reusable, corrosive homogeneous catalyst. Refer to the more general scheme, the combination of these characters in a heterogeneous catalyst in an organic reactions fulfill the principles of green chemistry, so called as green catalyst [4,14,15].

Previous works reported on the use of saponite and pillared saponite; however, their reusability has not yet been investigated [16,17]. With the use of different synthesis routes and schemes, the surface area of a pillared form is not as high as that of PCH. In other schemes, zinc catalyst is characteristically used in acid catalysis [18]. In order to explore the effectiveness of clay-based catalyst for citronellal conversion, this research aimed to prepare Zn supported on clay through pillarization (referred to as ZnO pillared saponite (Zn/PILS)) and Zn supported on PCH (Zn/PCH). Moreover, this research compared the catalytic activity of Zn/PILS and Zn/PCH in terms of physicochemical properties, particularly surface acidity and catalytic activity.

2. Materials and Methods

2.1 Materials

The clay mineral used to synthesize PCH

was saponite (Sumecton SA), which was obtained from Kunimine Industrial Company (Tokyo, Japan). Hexadecyltrimethylammonium bromide (CTMBr) (99%), isopropanol (99.9%), pyridine, trimethanolamine (TMA) (90%), tetraethylorthosilicate (TEOS) (98%), and zinc acetate dihydrate were purchased from Merck-Millipore (Germany), whereas citronellal (98%) and isopulegol (98%) were obtained from TCI (Tokyo, Japan).

2.2 Materials Preparation

Zn/PCH was prepared as follows: 2.5 g saponite was mixed with 9 g CTMBr (Aldrich) in 300 mL distilled water and then stirred overnight. TMA (0.88 g) was added into the suspension and then stirred for 24 h. The pillars were prepared by mixing 8.86 g zinc acetate dihydrate solution with 5 mL TEOS in isopropanol. The Zn content of PCH was set at 10 %wt. The suspensions were kept under hydrothermal condition in an autoclave at 100 °C for 24 h. Solids were obtained by filtering the suspension that was kept in the autoclave; the solids were washed with distilled water and ethanol and then air-dried at 60 °C for 12 h before being calcined at 500 °C for 2 h. The saponite was pillarized using similar procedure but without the addition of TMA and TEOS.

2.3 Material Characterization

Powder X-ray diffraction patterns of the samples were collected on a Rigaku Miniflex diffractometer equipped with Cu-K α radiation, and the diffractograms were recorded within the 2 θ range of 3°-80° with a step size of 0.02°. Surface parameters (Brunauer-Emmett-Teller (BET)) surface area, pore volume, pore distribution, and pore radius) were evaluated from the nitrogen adsorption-desorption isotherms at -77 K by an automatic ASAP 2020 system procured from Micromeritics (Norcross, GA, USA). Prior to the measurements, the samples were outgassed at 200 °C and at 10⁻⁴ mbar overnight. Surface areas were determined using the BET equation, whereas the pore distribution of materials were calculated using the Barrett-Joyner-Halenda equation. Elemental analysis was performed using a Phenom X instrument (Singapore). Surface acidity of the materials was analyzed through *n*-butylamine back titration, with acetic acid as standard.

2.4 Catalytic Activity Tests

Catalytic activity in citronellal isomerization was tested by using a Reflux system. A

catalyst (0.25 g; 100 mesh) was added into the citronellal solution in isopropanol (10 mL), and the mixture was refluxed for 3 h. The reactants and products were analyzed by a gas chromatograph–mass spectrometer (Shimadzu). Catalytic conversion and selectivity during isopulegol (Sisopulegol) production were calculated based on the peak change in citronellal, isopulegol, and other products (Equations (1) and (2)):

$$\text{Conversion} = \frac{A_{ci} - A_{ct}}{A_{ci}} \times 100\% \quad (1)$$

$$S_{iso} = \frac{A_{iso}}{A_{total} - A_{ct}} \times 100\% \quad (2)$$

With A_{ci} is peak area of citronellal in initial reactant, A_{ct} is peak area of citronellal in chromatogram of product, A_{iso} is peak area of isopulegol, and A_{total} is total peak area chromatogram of product. Catalyst reusability test was performed by filtering the catalyst after use followed by washing with ethanol and drying at 80 °C for 2 h.

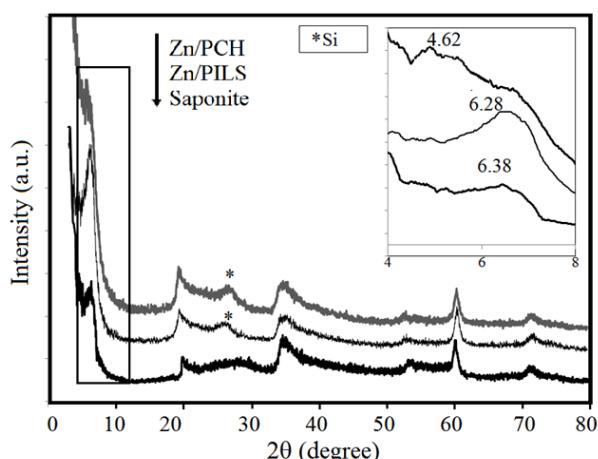


Figure 1. XRD pattern of materials.

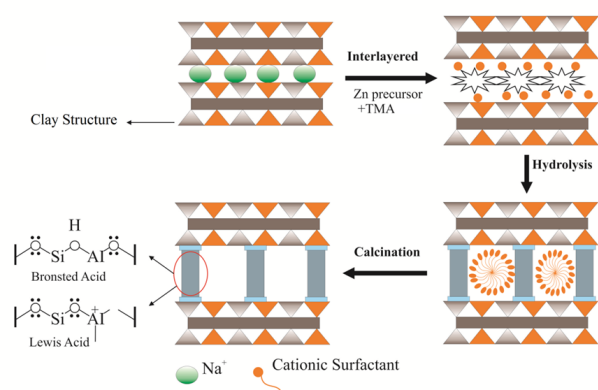


Figure 2. Schematic representation of PCH formation.

3. Results and Discussion

3.1 Physicochemical Characterization

Figure 1 and Table 1 show that the pillari- zation and PCH formation led to the increase in basal spacing d_{001} from 13.82 Å in saponite to a maximum of 14.73 Å in Zn/PILS and 19.08 Å in Zn/PCH. The increasing d_{001} pattern implies the formation of a space in the interlayer region, and this phenomenon was in turn influ- enced by another mechanism. The PCH for- mation is conducted due to the scheme in Fig- ure 2.

The formation of silica pillar after the inter- calation resulting from the use of surfactant prior to the entry ZnO into the intra-gallery creates a larger intra-gallery space. For both the Zn/PILS and Zn/PCH samples, a broad re- flection was observed at around 25° (*), indicat- ing the presence of silica in its elemental form in small amount and in its crystalline form, and this phenomenon is usually considered an effect of the formation of intra-gallery space during intercalation of the surfactant into a clay structure [20,21]. In this case, CTMA intercalation was utilized for both Zn/PILS and Zn/PCH formation. Data suggested the homo- geneous distribution of ZnO in the composite structure. The measured basal spacing is con- sistent with the TEM analysis results (Figure 3), suggesting that there are increasing grid- lines representing the sheet structure with the width of about 17-19 Å. This assumption is also consistent with the TEM image presented in Figure 3.

From the image, the formation of inter- gallery space is found as the lines formation in Zn/PCH which is absence in saponite samples, with the space identified at around 1.70-1.9 nm. The layered structures are appeared for saponite samples and by converting into Zn/ PCH, some spots exhibit the presence of ZnO

Table 1. Elemental analysis of materials.

Component	Composition (% at.)		
	Saponite	Zn/PILS	Zn/PCH
O	49.68	54.03	55.22
Na	3.23	1.09	0.03
Mg	8.3	9.18	7.18
Al	11.23	10.73	6.56
Si	27.51	19.69	17.65
Zn	0	5.28	6.52
C	-	-	6.05
N	-	-	0.79

particles. The presence of Zn in the modified saponite is confirmed by EDX analysis, and the spectra and data are presented in Figure 4 and Table 1, respectively. The amounts of Zn in both Zn/PILS and Zn/PCH are similar due to the similar molar ratio used in the preparation, and the values are lower than the approached amount (10 %wt).

According to a previous research on citronellal conversion involving a solid catalyst and the mechanism presented in Scheme 1, the acid-catalyzed isomerization is not only caused by protonic (H^+) species, but also by the presence of Lewis acidic species from the empty *d*-orbital provided by an active metal (in this case Zn).

Solid surface acidity represents the total Brønsted and Lewis acidities, and it was determined through pyridine adsorption followed by FTIR analysis (Figure 5). All samples demonstrated some absorption spectra related to the evolution of silica–alumina structure caused by the modification. All materials demonstrated the Si–O asymmetric stretching vibration and the Si–O–Si deformation vibration, and these vibrations upshifted to 1056 and 468 cm^{-1} , respectively. The presence of absorption bands at 2926 – 2946 cm^{-1} in the spectrum of PCH is associated with the rest intercalated template molecule which is specifically representing asymmetric and symmetric stretching vibrations of CH_2 groups. The presence of surface acid sites was identified from the three major absorption bands, namely, 1450 , 1490 , and 1545 cm^{-1} , which correspond to Lewis acidity, Brønsted and Lewis acidities, and Brønsted

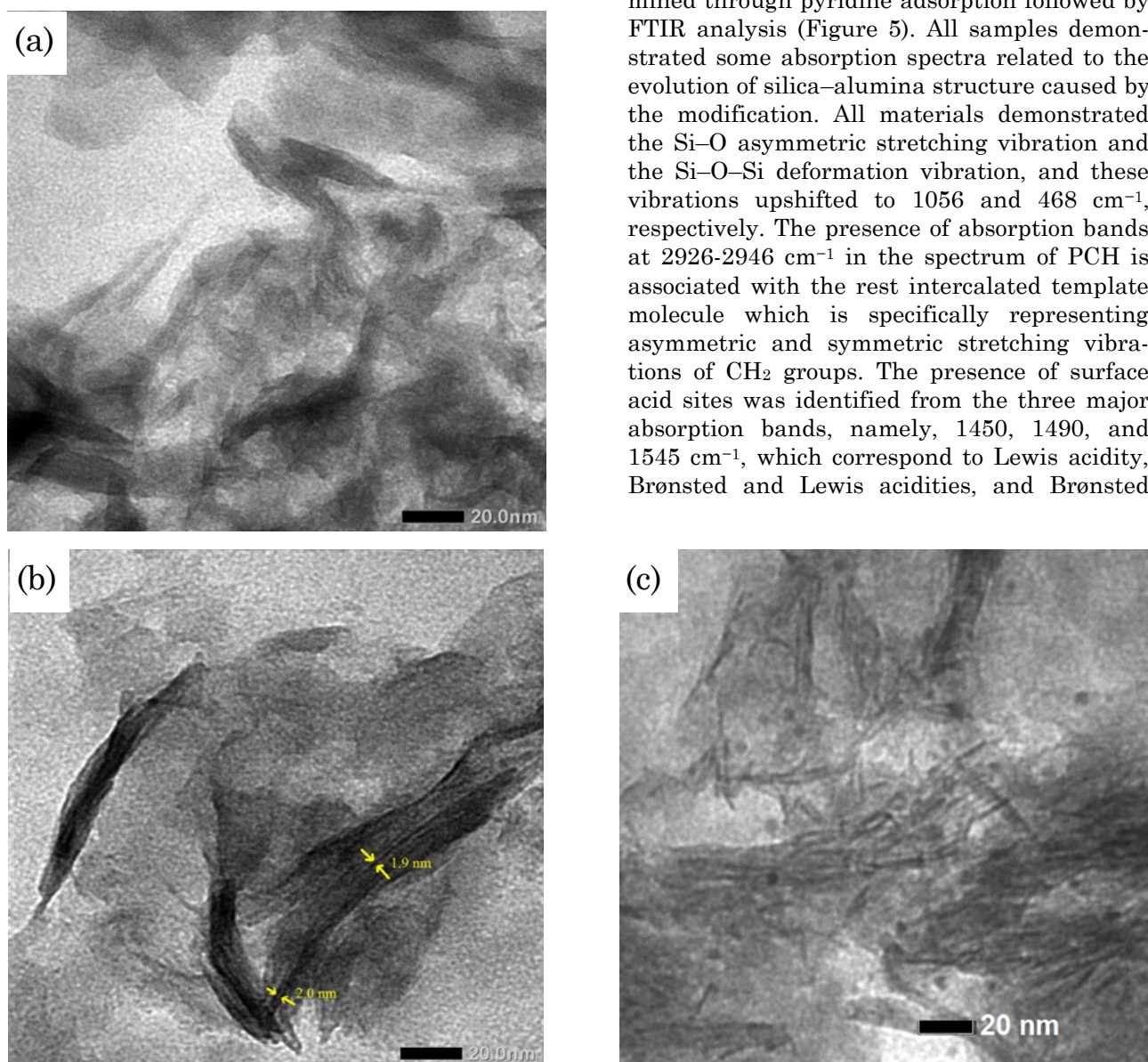


Figure 3. TEM profile of (a) Saponite (b) Zn/PCH-10 (b) Zn/PCH-30.

Table 2. Surface parameters and surface acidity.

Sample	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore radius (\AA)	Surface acidity (mol ethanolamine/g)
Saponite	110.12	0.0214	12.1	0.917
Zn/PILS	188.78	7.07×10^{-2}	17.88	1.152
Zn/PCH	770.22	0.7473	44.19	1.643

acidity. By comparing SAP, Zn-PILC and Zn/PCH, it is seen that Zn/PCH shows the more intensive spectrum as identification of both Brønsted and Lewis acid sites interaction with pyridine. The increasing surface acidity was also confirmed by the amount of surface acid sites as calculated by *n*-butylamine titration (Table 2). Moreover, the increasing surface acidity is consistent with the increasing specific surface area and pore volume as indicated by the adsorption-desorption profile (Figure 6a).

Table 2 shows the increasing specific surface area of saponite, and this trend is attributed to

both pillarization and PCH formation. Data show that pillarization increased the specific surface area by approximately two-fold; by contrast, the specific surface area of Zn/PCH increased by up to seven times with respect to that of saponite. The increasing specific surface area also corresponded with the increasing pore volume, which in turn was influenced by pore distribution (Figure 6b). The present values are similar to those reported for other metal-modified PCH prepared from saponite [9,21-25]. The increasing surface area and pore volume was due to the formation of intra-gallery space from intercalation and due to pillar formation from silica. Moreover, the presence of proton (H^+) from the framework formation enhanced the surface acidity. The increasing surface parameters and surface acidity contributed to the increasing catalytic activity as demonstrated in the kinetics of citronellal conversion (Figure 7).

Zn/PCH displayed a superior activity as shown in the kinetics of citronellal conversion, demonstrating that nearly all citronellal were converted into a product after 2 h of reaction.

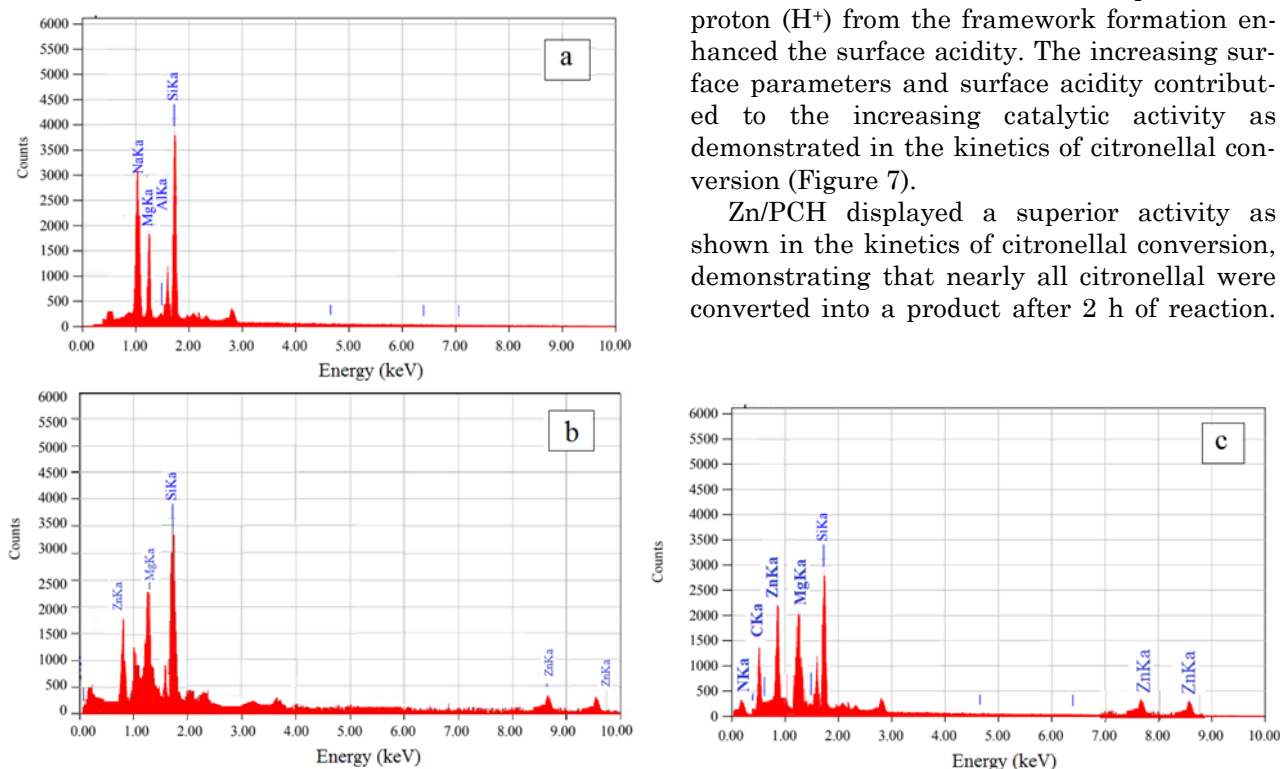


Figure 4. EDX spectra of (a) Saponite (b) Zn/PILS (c) Zn/PCH.

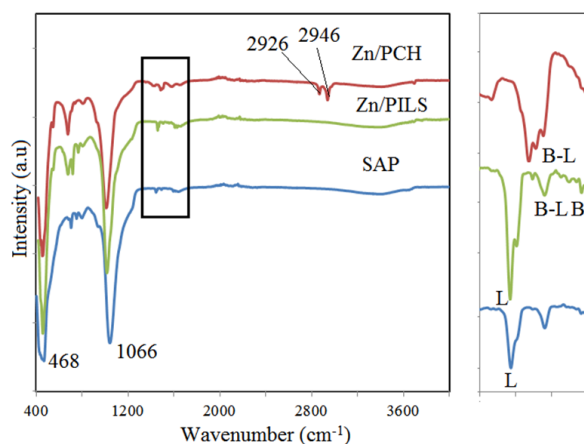
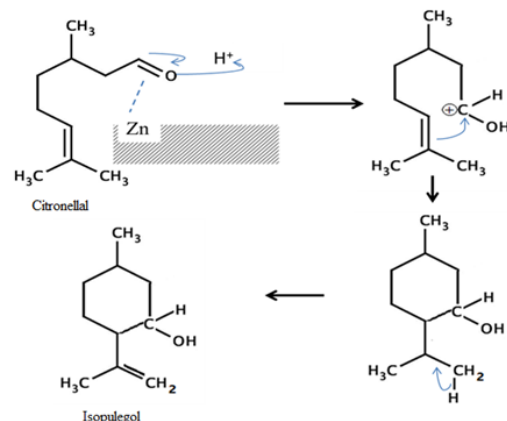


Figure 5. FTIR spectra of materials.



Scheme 1. Mechanism of citronellal conversion into isopulegol.

In addition, the activity of Zn/PILS was intermediate to the activities of Zn/PCH and saponite. All catalyzed reaction obeyed the pseudo-second order kinetics as shown by the fitness of the plot to Equation (3):

$$\frac{1}{C_t} = kt + \frac{1}{C_0} \quad (3)$$

where C_0 and C_t are the initial citronellal concentration and the citronellal concentration at time t , respectively, and k is the kinetics constant. The higher conversion rate is represented by the increasing kinetics constant from 0.003 /%h for saponite to 0.027 /%h for Zn/PILS and to an extreme extent of 43.22 /%h for Zn/PCH. However, the constant kinetics order suggested that the catalytic mechanism was not altered. Not only on the catalytic conversion, Zn/PCH also exhibits the isopulegol as

main product of the conversion, demonstrating that cyclization mechanism was the main mechanism involved in the reaction. The higher selectivity to produce isopulegol of the Zn/PILC catalyst compared with Zn/PILS is also in the same order with catalytic conversion, suggesting the role of the increasing specific surface area and surface acidity in the catalytic mechanism. The catalytic activity of Zn/PCH is comparable with that of clay-modified catalysts, such as sulfated zirconia-pillared montmorillonite, platinum dispersed on sulfated zirconia-pillared saponite, and nickel dispersed on sulfated zirconia-pillared saponite, which were used in previous citronellal conversion [16,26-28]. All of the above-mentioned catalysts that demonstrated high conversion rate was tested in a microwave-assisted conversion under tandem cyclization-hydrogenation, which is an in-

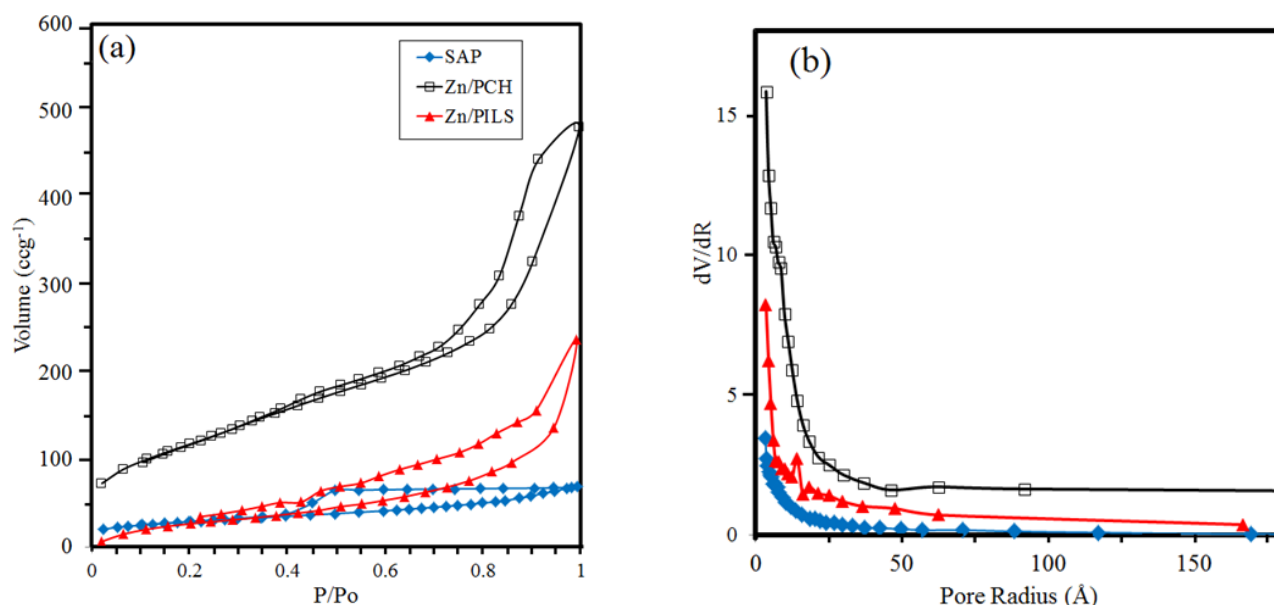


Figure 6. (a) Adsorption-desorption isotherm of materials, (b) Pore distribution of materials.

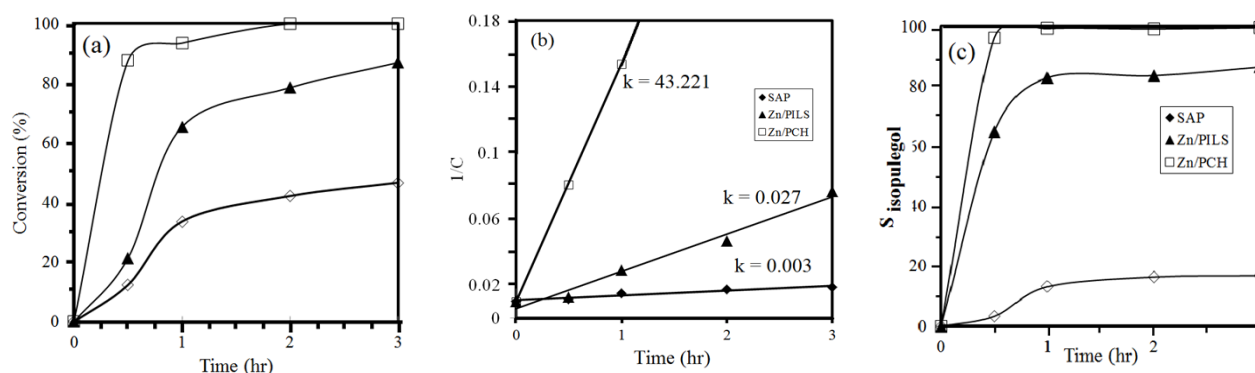


Figure 7. (a) Kinetics of citronellal conversion over varied catalyst, (b) pseudo-second order of kinetics, (c) Effect of reaction time on selectivity to isopulegol [catalyst weight: 0.15 g; citronellal: 5 mL; solvent: isopropanol].

tensive reaction mechanism. By contrast, the reaction system in this research was used only under reflux condition and without involving any other catalytic hydrogen transfer reagent. A selectivity of less than 100% represents other mechanisms wherein citronellal (1) conversion produces products other than isopulegol (2). GC-MS analysis results showed that there are two main by-products: menthone (3) and isomenthone (4). Both products are caused by the reductive condition in the conversion refer to the mechanism of citronellal conversion over Al/Fe-PIL (Scheme 2) [30].

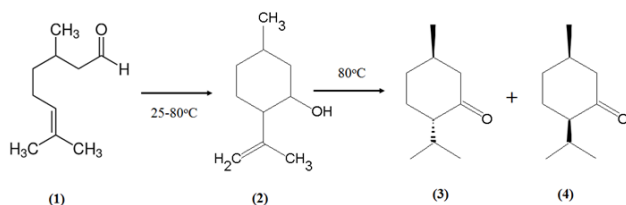
The reductive condition causing the production of menthone and isomenthone products may be attributed to the catalytic hydrogen transfer mechanism of citronellal conversion over nickel dispersed on zirconia-pillared saponite and over nickel dispersed on sulfated zirconia pillared montmorillonite [16,26]. By comparing the selectivity when Zn/PILC and Zn/PILS were used and by considering the specific surface area of the catalyst utilized in a previous work [30], one may probably attribute the lower selectivity to the less specific surface area that contributed to the lower reactant transport by the surface. This limitation in selectivity should be intensively studied for fur-

ther application. Furthermore, the effect of the reusability properties of Zn/PILS and Zn/PCH catalysts was studied by comparing the total conversion and the selectivity for isopulegol production, and the results are presented in Figure 8.

The comparison between the conversion during the first and second use showed that /PCH has the highest stability as shown by a relative same of conversion values, followed by Zn/PILS and then by saponite. In terms of selectivity for isopulegol production, the values were not influenced by recycling of both Zn/PILS and Zn/PCH, but the selectivity decreased for saponite. The presence of larger porous structure in Zn/PILS and Zn/PCH improves the possibility for reactivation. The results suggested that modification of a clay structure by a metal oxide renders stability to a heterogeneous catalytic conversion in an organic reaction.

4. Conclusion

Zn supported on clay by using pillarization mechanism (Zn/PILS)) and Zn supported on PCH (Zn/PCH) have been successfully prepared. Prepared materials show increasing specific surface area and solid acidity as consequent of the increasing basal spacing d_{001} from XRD analysis. Structural and textural studies showed that the insertion of the -pillars expand the original basal spacing of saponite to 19.08 Å, increasing specific surface area to 870 m²/g and increasing surface acidity for Zn/PCH. All physicochemical characters are in line with the enhancement on performance for catalyst ap-



Scheme 2. Mechanism of citronellal conversion using Al/Fe-PILC.

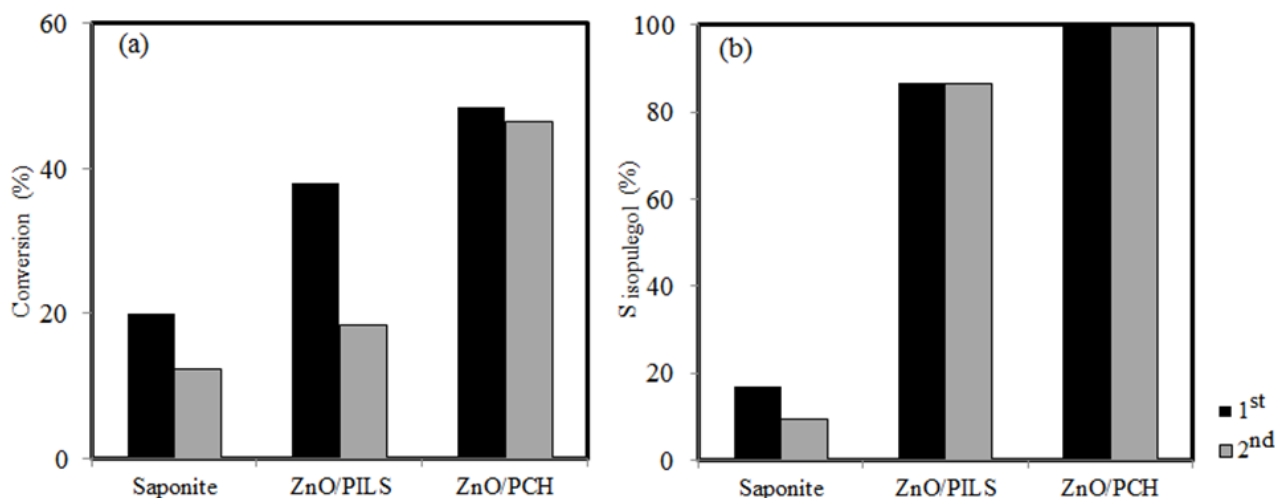


Figure 8. Comparison of fresh and recycled catalyst on (a) catalytic conversion, (b) selectivity in producing isopulegol.

plication for citronellal conversion into isopulegol. The increasing performance is shown by increasing the kinetics constant from 0.003/%h for saponite to 0.027 /%h and 43.22 /%h for Zn/PILS and Zn/PCH, respectively. Moreover, the reusability of the Zn/PCH catalyst is expressed by a relative unchanged total conversion and selectivity to produce isopulegol.

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