Microwave-assisted synthesized porous clay heterostructure-Zn/Si from montmorillonite for citronellal conversion into isopulegol

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Abstract
Microwave-assisted synthesis method was applied for producing porous clay heterostructure-Zn/Si heterostructure from Indonesian natural montmorillonite. The porous montmorillonite heterostructure was prepared by previously intercalating cetyl trimethyl ammonium as templating agent and surfactant, and trimethyl ammonium hydroxide as co-surfactant, followed by the introducing Zn–Si precursor solution for the sol-gel reaction of porous formation. The comparison of the use of microwave-assisted synthesis and hydrothermal method for the porous formation was studied. Physicochemical characterization by using XRD, SEM-EDX, TEM, gas sorption analysis, and FTIR method. Effect of the evolution of the surface characters on its catalytic activity in citronellal conversion into isopulegol was studied. The characterization by XRD informed the increasing basal spacing d001 from 1.57 nm into 3.71 nm by the microwave-assisted method, meanwhile the hydrothermal method produced 3.56 nm spacing. The increasing specific surface area from 98.82 m² g⁻¹ into 752.95 m² g⁻¹ and 409.95 m² g⁻¹ for microwave-assisted synthesized and hydrothermal synthesized composites, were obtained. These profiles are attributed to the increasing surface acidity determined by pyridine-adsorption method and n-butylamine titration method, and contributed to the significant increasing catalytic activity. The time-efficient synthesis method obtained by the microwave-assisted method is good alternative for the preparation of highly active montmorillonite heterostructure composite for acid-catalyzed organic reaction.

1. Introduction
Heterogeneous-catalyzed organic synthesis is one of popular technique developed in last decades due to the principles of green chemistry. The utilization of solid catalyst having high activity and recoverability minimizes the catalyst waste generally obtained by the use of homogeneous catalyst, and directly reduce the cost of the process by its reuse for several cycles. Many organic reactions over solid catalysts were reported and applied in industrial scale. Among several platform of organic synthesis, citronellal conversion into isopulegol is an important reaction. As chemical intermediate, isopulegol can be converted into several valuable chemicals in food and drug industries, such as menthol, ionone, etc [1]. For this reaction, highly acid catalyst is required. Within the heterogeneous catalyst scheme, many solid acid catalysts were designed and developed, which the basic idea is providing high specific surface area and capability to initiate cyclization mechanism by transferring solid acidity [2, 3]. For these purposes, modified material based on the solid supports such as zeolite, carbon, graphene, and mesoporous silica, and clay were reported.

Among these, porous clay heterostructure (PCH) is an interesting material, having possibility and challenges to be improved based on natural clay minerals. PCH is a semisynthetic material produced from clay through the
intercalation mechanism of silica material and the formation of intra-gallery of clay structure [4, 5]. The surface area of the PCH material which is usually ranging around 200–1000 m² g⁻¹, has properties to be high thermal stable, and capable to support surface reaction of heterogeneous catalysis mechanism. Fluorohectorite, montmorillonite, magadite, beidelite, saponite and vermiculite were reported to be used as initial precursors in PCH synthesis [6–8].

In order to improve surface characteristics and acidity, some metal oxide was applied for the PCH synthesis. Modification of clays into PCH with active metal oxides were reported to be effective to improve catalytic activity for some reactions such as alcohol dehydration, phenol wet peroxidation, esterification [9–11]. In addition, the exploration of PCH synthesis method is also important, refer to that the surface and catalytic properties of the PCH is strongly depending on the synthesis method and route. Some methods were applicable for optimizing the formation of mesoporous such as hydrothermal, solvothermal, or reflux method. For the consideration of greener and faster process, some methods for intensification were reported, for example ultrasound-assisted method and microwave-assisted method. Previous work reported the feasibility of ZnO-porous clay heterostructure synthesized from saponite mineral in the citronellal into isopulegol [12]. In fact, within similar class of clay; smectite, natural montmorillonite has same structure with synthetic saponite. The idea to use natural montmorillonite in PCH synthesis is a value-added scheme of material development. The comparison on synthesis method; microwave-assisted method and hydrothermal method was studied to look for optimization in the synthesis.

2. Materials and methods

2.1. Materials
Montmorillonite (Mt) was obtained from Pacitan, Wast Java, Indonesia. The sample was acid-activated prior use by refluxing in H₂SO₄ 1 N for 4 h followed by neutralization using H₂O. Chemicals consist of n-butylamine, zinc acetate, isopropanol, tetra ethyl ortho silicate (TEOS), cetyl trimethyl ammonium bromide (CTMA), tetramethylammoniumhydroxide (TMAOH) were purchased from Merck-Millipore (Germany). Methanol and n-hexane for gas chromatography were of HPLC grade and obtained from Merck-Millipore. Citronellal and isopulegol were purchased from Sigma (USA).

2.2. Preparation of PCH
PCH was prepared mixing 5 g of Mt with 3 g of CTMA in 300 ml of aquadest followed by stirring overnight. Into the mixture, 1 g of TMAOH, and the stirring was conducted for 4 h to get CTMA-Mt suspension. The pillaring agent was prepared by mixing zinc acetate and TEOS (at the Zn:Si molar ratio of 1:4) in 5 ml of isopropanol under vigorously stirring for 2 h. The pillaring agent was added into the CTMA-Mt suspension with the theoretical Zn content of 6% wt. The obtained mixture was then treated by hydrothermal method, and microwave-assisted method. For the hydrothermal method, the mixture was kept in an autoclave at 150 °C for 3 days, while for the microwave assisted method, the mixture was microwave-irradiated for 30 min. The gel obtained for each process was dried in an oven at 60 °C before calcination at 500 °C for 4 h, and the PCH samples were encoded as PCH/HT and PCH/MW for each hydrothermal synthesis method, and microwave-assisted method, respectively.

2.3. Material characterization
Material characterization was conducted by x-ray diffraction (XRD) analysis, scanning electron microscopy-energy dispersive x-ray (SEM-EDX), transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), Fourier-Transform Infra-Red (FTIR), and gas sorption analysis method. For XRD measurement, a Rigaku benchtop instrument was employed. Ni-filtered Cu Kα radiation (λ = 1.5406 Å) was utilized as radiation source, and the measurement was recorded in steps of 0.02° between 2θ=2° and 60°. SEM-EDX analysis was performed on Phenom X instrument (Singapore), while TEM analysis were collected on a JEOL 2010 (Tokyo, Japan). The specific surface area, pore volume, and pore radius investigation of the samples were measured on an ASAP 1200 instrument (Micromeritics, USA). In particular, the specific surface area was determined according to the Brunauer-Emmett-Teller (BET) method with nitrogen adsorption at 77.4 K with the degassing conditions of 150 °C for 2 h. X-ray photoelectron spectroscopy (XPS) was performed using a ULVAC instrument (Quanera SXM, Japan). Surface acidity of solids are conducted by pyridine adsorption method followed by FTIR measurements, and also quantitative n-butylamine titration method. For pyridine adsorption method, the materials were evacuated by vacuum pump for 1 h before pyridine vapor exposing for 4 h, and then reevacuated for 1 h before analyzed using AVATAR FTIR spectrophotometer (Singapore). Total acidity of the samples was measured using a potentiometric method of titration with n-butylamine. N-Butylamine solution (0.1 N; 0.5 ml) was added to the dispersion of 0.2 g samples in acetonitrile solvent,
followed by stirring for 3 h. The unadsorbed n-butylamine was determined by potentiometric titration monitored on Hanna PH210. The total acidity was calculated based on the amount of adsorbed n-butylamine for corresponding mixture.

Catalytic activity of the synthesized materials was tested in citronellal conversion into isopulegol based on following reaction (figure 1):

The experiments were varied into two methods: Reflux method, and microwave-assisted method. A modified-commercial microwave oven (Frequency of 2469 Hz) was employed.

The catalytic conversion of citronellal was performed by using reflux method and microwave-assisted method. The reaction conversion (C/%) and selectivity to produce isopulegol (Siso/%) were determined based on GCMS analysis by following equations (equations (1)–(2)):

$$\text{C} = \frac{[\text{citronellal}]_0 - [\text{citronellal}]_t}{[\text{citronellal}]_0} \times 100\%$$

$$\text{C} = \frac{[\text{isopulegol}]}{[\text{Product of reaction}]} \times 100\%$$

Concentration of citronellal and isopulegol were detected on Gas Chromatography-Mass Spectrometry (GCMS) Shimadzu (Tokyo, Japan).

3. Results and discussion

3.1. Physicochemical character of materials

The structural changes during the synthesis of PCHs are indicated by XRD patterns showed in figure 2. The Mt sample shows the diffraction peak $d_{001}$ attributed to the layered structure positioned at $5.62^\circ$, corresponding to the basal space of 1.56 nm. Other diffractions are related with the two-dimensional diffractions $hk$ found at $19.75^\circ$ and $35.04^\circ$ which are assigned to the summation (02) and (11) indices, and (13) and (20) indices, respectively. After the modification into porous clay heterostructure formation, the $d_{001}$ reflection is shifted to
lower values of 2θ angles at about 2.36° and 2.46° corresponding to the basal spacing at 3.71 nm and 3.56 nm for PCH/MW and PCH/HT, respectively.

These data indicated interlayer expansion which attributed to formation of intra-gallery silica-zinc oxide pillars which stacked-together within the clay layers. The expanded basal spacing is also identified by TEM image in figure 3. The wider space of layered structures which are ranging from 1.9–3.7 nm are appeared for the PCH samples, meanwhile it is not clearly represented in Mt sample. These textural changes are characteristic for PCH [13, 14]. Moreover, the PCH/HT shows the ordered structure characteristics for the porous surface, as representation of mesoporous formation [8, 15].

These changes are in line with the increasing N\textsubscript{2} adsorption–desorption profile of materials with the increasing calculated surface parameters of BET specific surface area and pore volume. As seen from the isotherm (figure 4) and calculated parameters listed in table 1, the PCH samples exhibit higher adsorption capability at along P/P\textdegree\textsubscript{0} values, which represented by the increasing specific surface area from 98.82 m\textsuperscript{2} g\textsuperscript{−1} in Mt to be 752.95 m\textsuperscript{2} g\textsuperscript{−1} for PCH/MW and 405.95 m\textsuperscript{2} g\textsuperscript{−1} for PCH/HT. The pore distribution in figure 3(b) confirms the pore evolution which convert from microporous in Mt into mesoporous formation in PCH samples. The PCH/MW represents two dominant pore radii; 12 Å and 19 Å, meanwhile PCH/HT has the dominant pore at 12 Å, which are ranged in mesoporous size distribution.

The coexistence of porosity is also remarkably confirmed by surfact profile identified by SEM image in figure 5. The flaky structures are exhibited by PCH samples along with a thistle-like structure which is characteristics for the two-dimensional ZnO nanoparticles surface [16–18]. The elemental analysis based on EDX spectra recorded about 5% at. Zn in both PCH samples along with the increasing Si content due to the addition of silica from TEOS (table 2).

The existence of zinc oxide formation in the PCH samples is justified by XPS measurement with the spectra presented in figure 6. The survey scan of PCH/MW sample (figure 6(a)) reveals Zn peaks in addition to the O (531.47 eV), Si (103 eV), and Al (75.6 eV) some Auger peaks of Zn. The presence of Zn is identified by the doublet peaks ascribed to Zn 2p\textsuperscript{3/2} and 2p\textsuperscript{1/2} core levels (figure 6(b)), representing the the presence of Zn\textsuperscript{2+} ions in an oxide environment. In addition, the deconvolution of O1s peak exhibits peak at 531 eV and 532.4 eV which are corresponding to the O–H and Zn–O spectral area (figure 6(c)) [7, 19, 20].

The FTIR spectra (figure 7) show intense absorption spectra at around 3500–3600 cm\textsuperscript{−1} which represent the OH stretching region in Mt and PCH samples. The bands located at 3646 cm\textsuperscript{−1} corresponds to the sum of several bands within 3756–3525 cm\textsuperscript{−1} range which has been classically ascribed to the oxygenation stretching from the 2:1 layers. The bands at 3200–3350 cm\textsuperscript{−1} are assigned to the absorbed molecular water absorption [21–23].
This representation is also in line with the identification of surface acidity by using pyridine-adsorption method. The FTIR spectra of pyridine-adsorbing materials (figure 8) depicts the effect of Zn incorporation in the PCH samples as shown by the more intense pyridine spectra at 1450 cm\(^{-1}\) and 1540 cm\(^{-1}\), respectively. Each spectrum is associated with the Lewis and Broensted acidity refer to the interactions presented in figure 8(a).

Quantitatively, the ratio of Lewis to Broensted acidity (L/B) calculated by the ratio of the transmittance values (equation (3)) is listed in table 1.

\[
\frac{L}{B} = \frac{\text{Intensity of absorption at } 1450 \text{ cm}^{-1}}{\text{Intensity of absorption at } 1540 \text{ cm}^{-1}}
\]  

\[\text{(3)}\]

Table 1. Surface parameter of materials.

| Surface parameter                      | Mt       | PCH/MW   | PCH/HT   |
|----------------------------------------|----------|----------|----------|
| BET specific surface area (m\(^2\) g\(^{-1}\)) | 98.82    | 752.95   | 409.95   |
| Pore volume (cc g\(^{-1}\))            | 9.89 \times 10\(^{-3}\) | 5.24 \times 10\(^{-2}\) | 2.01 \times 10\(^{-2}\) |
| Pore radius (Å)                        | 6.78     | 11.2     | 18.7     |
| Total acidity (meq n-butylamine g\(^{-1}\)) | 0.68     | 1.48     | 1.84     |
| L/B                                    | 0.98     | 4.33     | 2.27     |
The influence of Zn in the formation of porous clay heterostructure implies the enhanced L/B ratio, which means either the more Zn-pyridine interaction, or Si–O-pyridine interaction rather than the H-pyridine interaction. It is also confirmed by the higher surface acidity of PCH samples compared to Mt calculated by n-butylamine titration method. Generally speaking, the porous clay heterostructure formation generates the increasing specific surface area due to the formation of intra-gallery of the silica-alumina sheets, which directly accommodates the surface acidity [24].

Remarkably, the microwave-assisted synthesis produced the higher performance porous clay heterostructure with more time-efficient procedure. Under microwave-irradiation, the interaction among molecules for the formation of silica-zinc porous structure is more intensive due to the activated of internal vibration energy. The faster time of intercalation by this intensification was also reported by previous works on clay pillarization [10, 25, 26].

**Table 2.** Elemental analysis based on EDX analysis of materials.

| Element         | PCH/MW % at. | PCH/HT % at. | Mt % at. |
|-----------------|--------------|--------------|---------|
| Oxygen          | 63.16        | 64.8         | 56.8    |
| Silicon         | 20.47        | 21.38        | 23.15   |
| Aluminium       | 6.65         | 7.34         | 14.2    |
| Zinc            | 5.19         | 5.29         | 0       |
| Iron            | 3.93         | 2.65         | 5.29    |
| Magnesium       | 0.6          | 0.54         | 0.56    |
3.2. Catalytic activity of material
The increased surface acidity is aimed to enhance the catalytic activity in citronellal conversion into isopulegol refer to following equations (1)–(2). The data are listed in table 3.

The result in table 3 clearly indicated that conversion of citronellal and selectivity to produce isopulegol increase by the use of PCH samples catalysts in both reflux and MW-assisted reaction. The comparison on is attributed to the increasing specific surface area and the availability of active sites as indicated by the higher conversion by PCH/MW rather than PCH/HT. The presence of zinc atom as Lewis acid sites together with H+ from the hydroxyl of the PCH structure as Broensted acid sites contribute to conduct the isomerization reaction.

The Lewis acidity plays role to coordinate with double bond and carbonyl group in citronellal molecule along with rearrangement in the presence of the Broensted acid sites. The role of both acid sites in the mechanism is also proven by solvent-less microwave-assisted reactions (experiment 7–13). The 100% conversion obtained by utilization of PCH/MW implies that acidity transfer mechanism can proceed without solvent as transport media. It can also be concluded that reaction time does not significantly affect to the either conversion and selectivity to produce isopulegol. These data represent that both PCH samples have higher activity compared with Ni–Zr/montmorillonite, sulfated-Ni/montmorillonite in similar reaction method [12].

4. Conclusion
Microwave-assisted synthesis of porous clay heterostructure of montmorillonite-ZnO/silica from natural montmorillonite was successfully conducted. The work demonstrates the feasibility of microwave-assisted method for intensification of zinc-silica pillars formation in the intra-gallery structure of montmorillonite. The
porous composite exhibited the increasing surface profile identified by the increasing basal spacing $d_{001}$ of montmorillonite structure, the formation of porous surface, and creating mesoporous distribution. These enhancements provide the more surface acidity. The higher Lewis to Brønsted surface acidity ratio obtained by the presence of ZnO in the composite. The comparison on microwave-assisted method with hydrothermal method revealed the higher $d_{001}$ basal spacing expansion as well as the higher specific surface area of the composite heterostructure. The increasing surface profiles play role in the increasing catalytic activity in citronellal conversion into isopulegol, either by Reflux or by microwave-assisted method. The higher specific surface area and surface acidity contributes to the higher conversion and selectivity to produce isopulegol. The faster time to synthesis with the higher surface characteristics of microwave-assisted synthesis method is

Figure 8. (a) Lewis acid interaction and Broensted acid interaction in pyridine adsorption (b). FTIR spectra of pyridine-adsorbed materials.
promising for the preparation of highly active montmorillonite heterostructure composite for acid-catalyzed organic reaction.

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Table 3. Catalytic conversion and selectivity to produce isopulegol by prepared materials in varied reaction condition.

| Exp | Reaction condition-time | Catalyst-Solvent | Catalyst dosage (mg/5 ml) | C(%) | S_(C6H10)(%) |
|-----|------------------------|-----------------|--------------------------|-----|-------------|
| 1   | Reflux-1 h             | Mt-isopropanol   | 0.25                     | 83.00 | 45.60       |
| 2   | Reflux-1 h             | Mt-isopropanol   | 1                        | 83.00 | 56.7        |
| 3   | Reflux-1 h             | PCH/MW-isopropanol | 0.25                | 83.00 | 100.00      |
| 4   | Reflux-1 h             | PCH/MW-isopropanol | 1                      | 83.00 | 100.00      |
| 5   | Reflux-1 h             | PCH/HT-isopropanol | 0.25                 | 83.00 | 23.55       |
| 6   | Reflux-1 h             | PCH/HT-isopropanol | 1                      | 83.00 | 25.4        |
| 7   | MW-15 min              | Mt-no solvent    | 0.25                     | 83.00 | 68.50       |
| 8   | MW-5 min               | PCH/MW-no solvent | 0.25                    | 83.00 | 100.00      |
| 9   | MW-10 min              | PCH/MW-no solvent | 0.25                    | 83.00 | 100.00      |
| 10  | MW-15 min              | PCH/MW-no solvent | 0.25                    | 83.00 | 100.00      |
| 11  | MW-5 min               | PCH/HT-no solvent | 0.25                    | 83.00 | 100.00      |
| 12  | MW-10 min              | PCH/HT-no solvent | 0.25                    | 83.00 | 100.00      |
| 13  | MW-15 min              | PCH/HT-no solvent | 0.25                    | 83.00 | 100.00      |
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