

Unravelling Physicochemical Features and Catalytic Activity of Microwave-Assisted Prepared ZnO-SiO₂-Pillared Montmorillonite for Acid-Catalysed Citronellal Cyclization

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Abstract

Microwave-assisted preparation of bimetal ZnO-SiO₂-pillared montmorillonite using Indonesian natural montmorillonite has been performed. The preparation was proceeded by directly dispersion of zinc oxide and tetraethyl ortho silicate as silica precursors into montmorillonite suspension with tetramethyl ammonium hydroxide followed by microwave irradiation. The effect of zinc content in the nanocomposite was studied by investigating the structure, surface textural, and surface acidity by employing x-ray diffraction (XRD), scanning electron microscopy-energy dispersive x-ray (SEM-EDX), gas sorption analysis, and pyridine adsorption-Fourier-transform Infra-Red (FTIR) method. The results of characterization notified the increasing basal spacing d_{001} of montmorillonite from 1.27 nm into 2.72 nm and 2.43 nm for zinc content of 5 mmol/g and 10 mmol/g, respectively. The higher zinc content is attributed to the increasing specific surface area and surface acidity which contributed to the significantly increasing catalytic activity. The conversion of 99.99% and selectivity to produce isopulegol of 66.39% were achieved as optimum activity of the time-efficient prepared pillared montmorillonite.

Keywords

Acid Catalysis, Citronellal, Cyclization, Pillared Clay

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1. INTRODUCTION

Citronellal conversion into isopulegol is one of the important routes in chemical industries as isopulegol significantly plays role in the fragrance, flavor, pharmaceutical, and fine-chemical industries. As an example, isopulegol is recognized as a valuable intermediate for the production of menthol, mean while it has a high-demand market utilized in pharmaceuticals, personal case, toiletries, and food products (Venancio et al., 2026). Citronellal to isopulegol reaction is a cyclization reaction facilitated by acid catalyst, either Lewis or Brønsted acids (Mäki-Arvela et al., 2023). In the green chemistry and technology perspective, development on the effectiveness of the reaction by considering environmentally sustainability leads to the use of heterogeneous acid catalytic reaction systems. Previous works notified the capability of clay-based acid catalysts for the reaction with the advantageous particularly on easy in product's separation and reusability.

Bentonite or montmorillonite clay modification with metal oxide such as ZnO, ZrO₂, and TiO₂ exhibited an improved acid-site density, surface area, pore structure, and stable acid sites that are crucial for governing citronellal conversion into isopulegol (Fatimah et al., 2015, 2016; da Costa et al., 2021; Shah et al., 2019). Modification with silica in the form of silica-pillared montmorillonite expressed the enhanced physicochemical features and catalyst stability. In other side, zinc oxide-based catalyst demonstrated the surface acidity enhancement. Based on previous research, combination of silica-pillared clay, especially montmorillonite clay, with other metal oxide could appreciably enhance the physicochemical features and catalytic performance (Hu et al., 2026). Previous work presented the time-efficient procedure of ZnO-dispersed onto porous clay heterostructure (PCH), which is technically performed in two steps: the formation of PCH by the formation of silica interlayers, followed by ZnO dispersion by impregnating zinc precursors.

Intensification is still a challenge in the preparation of montmorillonite-based catalyst, such as the use of microwave (MW) irradiation in the dispersion process. High energy of MW intensively accelerates crystallization, oxidation, and porous formation (Labib et al., 2020; Rustembekkyzy et al., 2024). Although ZnO-dispersed porous clay heterostructure for citronellal conversion into isopulegol has been reported (Rubiyanto et al., 2020), a strategy of binary metal oxides pillarization towards montmorillonite with studying the influence of zinc content towards catalytic activity, has not been studied yet. Referred to previous works on binary metal oxide pillarization together with silica, hypothetically, the binary metal oxide pillarization towards montmorillonite could enhance the stability of dispersed ZnO to support its catalytic activity (Dincer et al., 2020; Najafi et al., 2022). Different from the porous clay heterostructure (PCH), the bimetal oxide pillarization is prepared by directly ion-exchange process with a mixture of the zinc and silica precursors without additional surfactant, while in the PCH formation, silica pillars within the interlayer regions of clay structure is formed by utilizing templating agent such as a combination of cetyl trimethyl ammonium (CTMA) and trimethanol ammine (TMA) followed by the dispersion of zinc oxide precursor. The PCH has a mesoporous structure, while bimetal pillaring tends to form microporosity. With the bimetal oxide pillarization approach, a simpler procedure and, in addition the use of MW irradiation become the novelty of this work.

Using different schemes of the nanocomposite formation, the aim of this research is to study the preparation of bimetal zinc oxide-silica-pillared montmorillonite (ZnO-SiO₂/Mt) using MW intensification. The main emphasis of the research is on the physicochemical properties of the material that support the catalytic activity, as studied by kinetic study.

2. EXPERIMENTAL SECTION

2.1 Materials

The chemicals used in this study were tetraethyl orthosilicate (TEOS), zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, 99%, Merck), sodium hydroxide (NaOH, 95%, Merck), citronellal (90%, TCI), isopulegol (95%, TCI), tetramethylammonium hydroxide (TMAOH) (95%, Merck), and isopropanol ((CH₃)₂CHOH, 95%, Merck). Natural montmorillonite originated from Pacitan, East Java, was purchased from online market in Indonesia.

2.2 Preparation of Materials

The materials of ZnO-SiO₂/Mt was prepared in two steps: (i) the formation of montmorillonite suspension, (ii) pillarization using ZnO and SiO₂ precursors. Firstly, about five grams of Montmorillonite and 5 mL of TMAOH were dispersed in 100 mL of deionized water followed by stirring at room temperature overnight. The binary metal precursor was prepared by mixing zinc acetate and TEOS in isopropanol as the solvent. The molar ratio of Zn was varied at 5 mmol/g and 10 mmol/g, and Si molar to montmorillonite mass ratio was 5 mmol/g. The precursor was slowly added to the suspension under rigorous stirring, and as homogeneous dispersion was achieved, the mixture was MW

irradiated for 30 min. The MW radiation was at a frequency of 2.45 GHz and the power of 100 Watt. The obtained suspension was then filtered followed by washing using 1 L of DI water. The solid was dried in an oven at 105 °C overnight prior to the calcination at 600 °C for 3h. With the varied Zn content of 5 mmol and 10 mmol, the obtained materials are encoded as 5ZnO-SiO₂/Mt and 10ZnO-SiO₂/Mt, respectively. The schematic procedure of the synthesis is presented in Figure 1.

2.3 Physicochemical Characterization

The XRD spectrum of the prepared samples and raw montmorillonite were recorded using X-ray diffractometer (D Philips: PW1800) with Ni-filtered Cu- K α radiation (λ = 1.5418 Å), 45 kV, 40 mA and a scan rate of 0.02 °/s in the region of (0 - 75) 2 θ . The morphology and elemental analysis were performed on scanning electron microscopy-energy dispersive x-ray (SEM-EDX) model JEOL.JEM- 6360. Surface textural analysis was conducted based on nitrogen adsorption-desorption at using a Micromeritics ASAP 2010 apparatus. The N₂ adsorption was performed at 77K after the samples were degassed at 120 °C for 4 h at a degassing pressure of 10⁻³ mbar. Total acidity of the samples was measured using a potentiometric back titration method. About 0.2 g of the solid sample was dispersed in n-butylamine solution (0.1 N; 5 mL) followed by stirring for 15 h. The filtration was carried out to suspension, and the obtained filtrate was titrated with an acetic acid solution as standard to determine the remaining base. Total acidity was calculated as the amount of adsorbed n-butylamine per gram of the sample. Besides the total acidity, surface acid distribution was studied by pyridine adsorption followed by Fourier-Transform Infra-Red (FTIR) analysis on Perkin Elmer instrument. The samples were dried in an oven Prior to being kept in a closed desiccator with pyridine solution exposure and placed in an open chamber overnight. The FTIR analysis was conducted to the adsorbed samples after evacuation.

2.4 Catalytic Activity Evaluation

Catalytic activity of the prepared materials was evaluated in citronellal conversion into isopulegol based on following reaction (Figure 2). Particularly, about 0.2 g of catalyst was mixed with 10 mL of citronellal and 10 mL of isopropanol as solvent. The Reflux was proceeded at varied time of reaction, 1, 2 and 3 h at temperature of 80 °C. The results of the reaction were analyzed using gas chromatography-mass spectrometry (GCMS). GC-MS Shimadzu QP2020 with HP5 column was employed for the analysis. The technical conditions for analysis are the use of argon as gas carrier, injection volume of 1 μ L, the flow rate of 1.0 mL/min, and the injector temperature of 250 °C.

The reaction conversion (C(%)) and selectivity to produce isopulegol (S_{iso}(%)) of the reaction were determined based on GCMS analysis by following equations (Equations (1)-(2)):

$$C(\%) = 100\% \times \frac{[\text{citronellal}]_0 - [\text{citronellal}]_t}{[\text{citronellal}]_0} \quad (1)$$

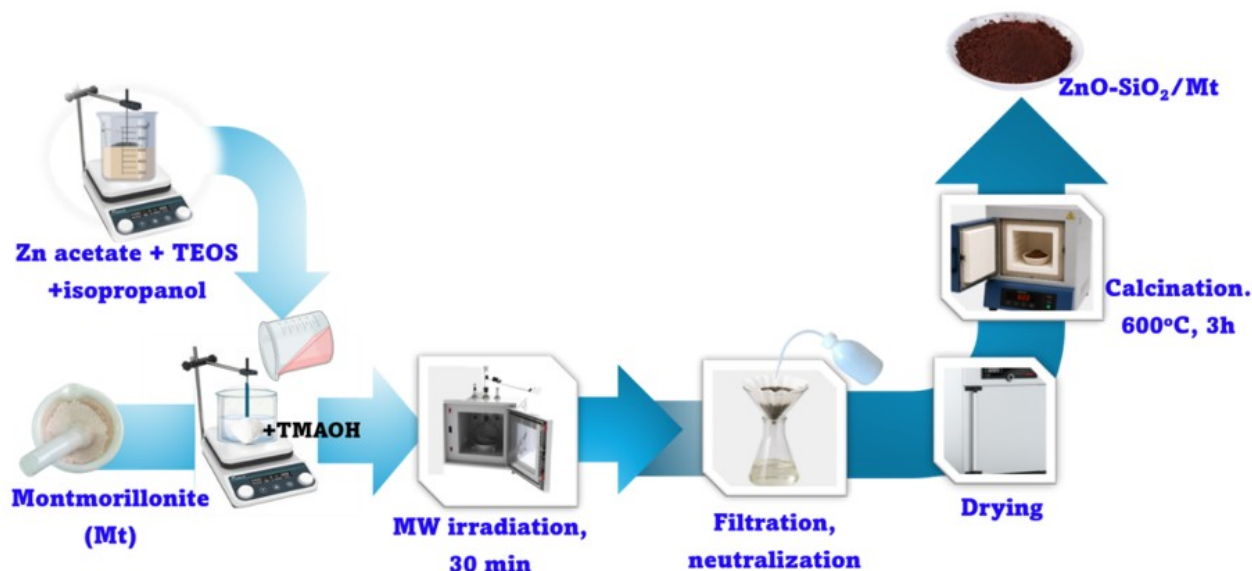


Figure 1. Scheme of Material's Synthesis Procedure

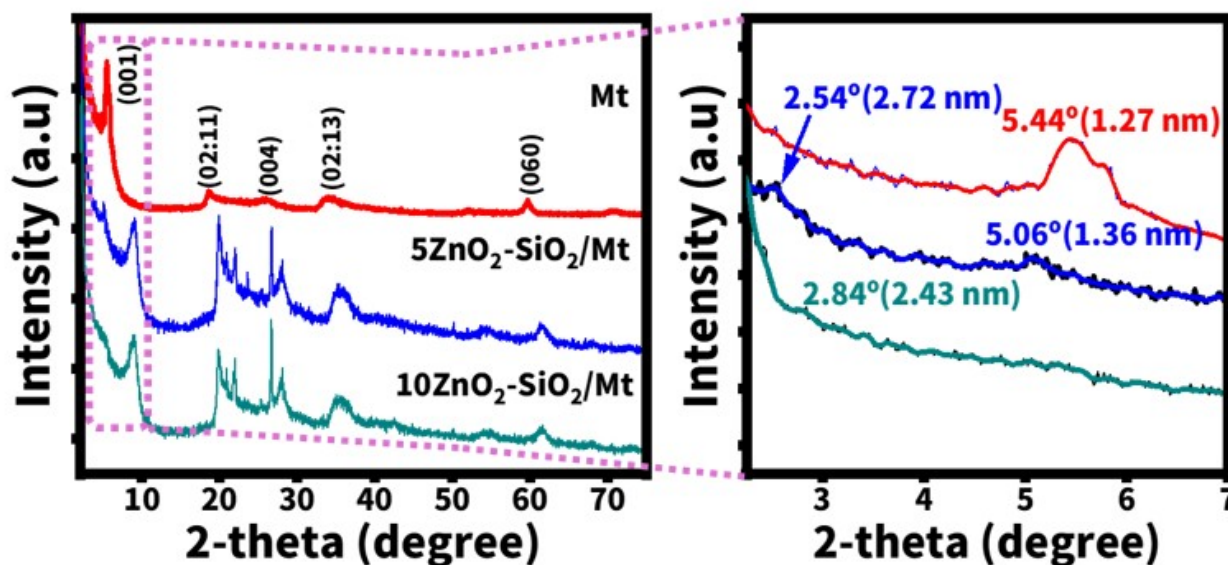


Figure 2. XRD Pattern of Prepared Samples

$$S_{iso}(\%) = 100\% \times \frac{[isopulegol]}{[Product\ of\ reaction]_0} \quad (2)$$

where $[citronellal]_0$ and $[citronellal]_t$ are the concentrations of citronellal at the initial and at time of t , and $[isopulegol]$ is the concentration of isopulegol. The concentrations of citronellal and isopulegol were determined using the external standard method. Pure citronellal and isopulegol were analyzed under the same conditions; then the peak area was used to measure the concentration of analytes.

3. RESULTS AND DISCUSSION

3.1 Material's Properties

XRD pattern of the prepared materials compared to pristine montmorillonite (Mt) is presented in Figure 2. The Mt shows the characteristic (001) basal reflections positioned at 5.44° associated to the plane distance of 1.27 nm. The other reflections associated with (002) and (060) are exhibited at 26.04° and 59.68°, respectively. In addition, there are three two-dimensional bands, (02;11) at 18.58° and (20;13) at 34.43° that are characteristics of the montmorillonite structure (Qi et al., 2008). After modification using ZnO and SiO₂, there are the maintained reflections with



Figure 3. Schematic Representation of Pillarization and Formation of Uniform Interlayer's Distance

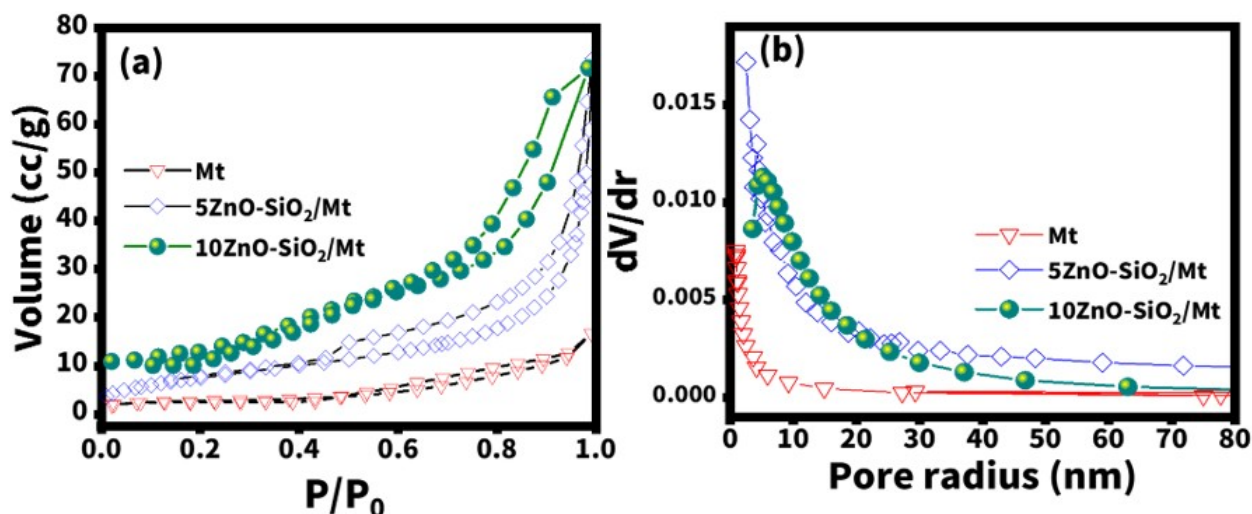


Figure 4. Adsorption/Desorption Isotherm (b) Pore Size Distribution of the Prepared Samples

Table 1. Textural Parameters Based on N₂ Adsorption/Desorption Isotherm

Sample	BET specific surface area (m ² /g)	Pore volume (cc/g)	Pore radius (nm)
Montmorillonite (Mt)	76.02	0.12	6.9
5ZnO-SiO ₂ /Mt	105.39	0.65	9.4
10ZnO-SiO ₂ /Mt	188.78	1.14	9.5

the shifting peaks. Similar to the identification on enhanced interlayer region of layered structure, the occurring pillarization is demonstrated by the shifting of d_{001} reflection into lower angle (Abriyanto et al., 2024). The basal spacing d_{001} peak was shifted to 5.06° and 2.54° in 5ZnO-SiO₂/Mt associated to the spacing of 1.36 nm and 2.72 nm, respectively. With a higher zinc content in 10ZnO-SiO₂/Mt, the peak is shifted to 2.84° which is appropriate to the spacing of 2.43 nm. The achievable pillar oxide spaces by the bimetal pillarization is higher compared to zinc oxide-pillared montmorillonite reported by previous works with d_{001} of 1.62 nm (Fatimah et al., 2011) and 1.53 nm (Hur et al., 2006). However, both modified samples demonstrate lower intensity as an indication of low crystallinity of the peaks, suggesting that

the insertion of ZnO and SiO₂ is not homogeneously distributed within the interlayer space of clay. Figure 3 is the schematic representation of the possible structure. Non-homogeneous dispersion leads to non-uniform interlayer space distances, which in many cases are represented as a house-of-cards structure (Fatimah et al., 2021).

The change in interlayer space distance is confirmed by the N₂ adsorption/desorption isotherm (Figure 4) which represents the pore radius distribution and the textural parameters of BET specific surface area, pore radius and pore volume (Table 1). The modification enhances adsorption/desorption capacity by modification as shown by the higher adsorbed volume at all P/P^0 range, associated with the higher pore size distribution. The

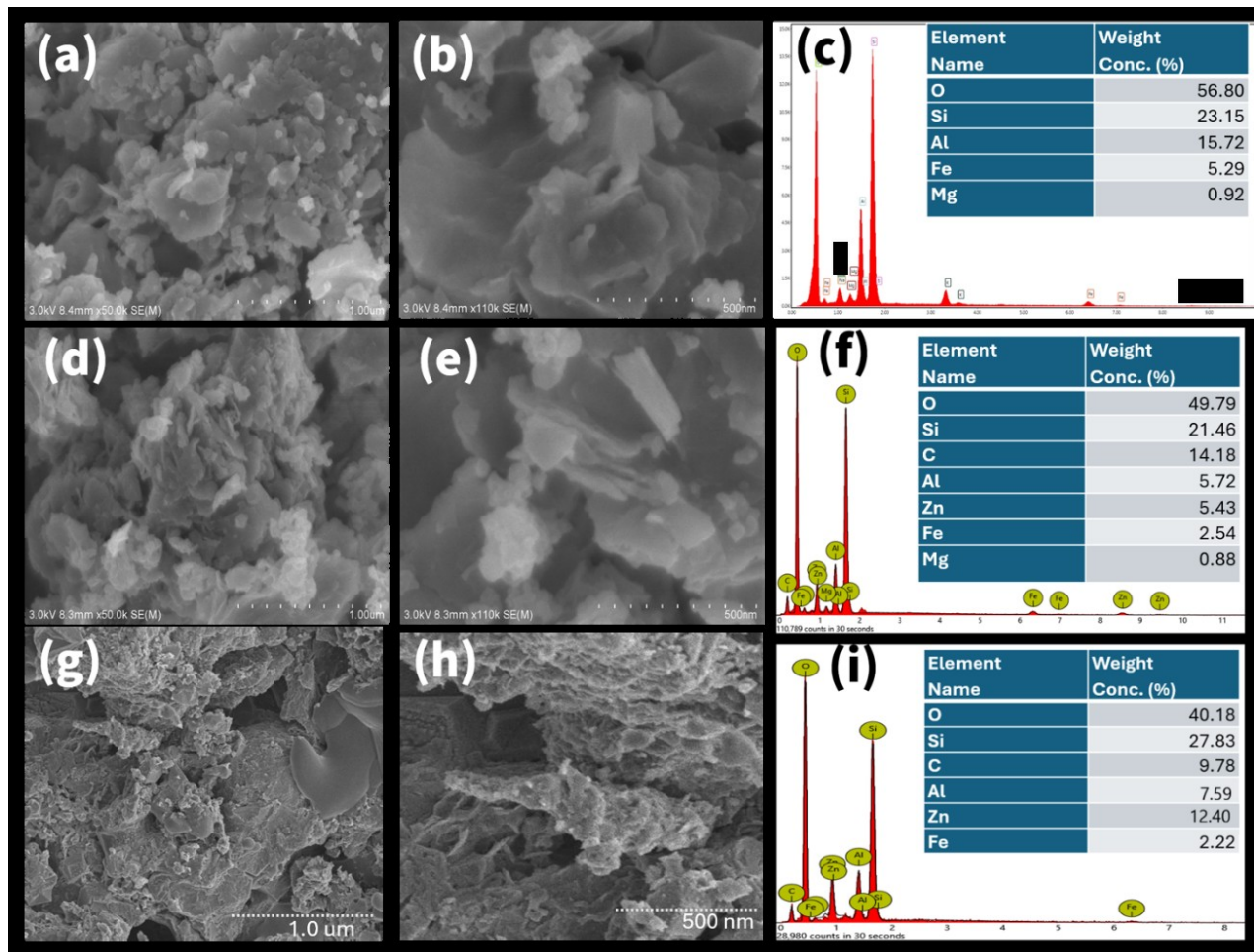


Figure 5. SEM Images at Different Magnification and EDX Spectrum of (a-c) Mt, (d-f) 5ZnO-SiO₂/Mt, (g-i) 10ZnO-SiO₂/Mt

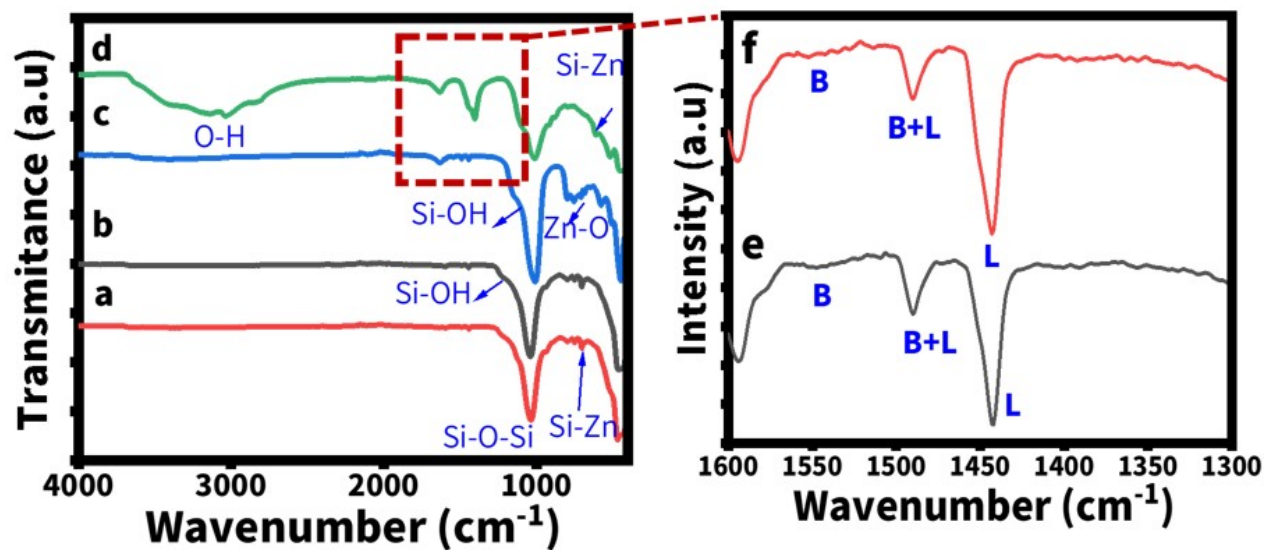


Figure 6. FTIR Spectra (a) 5ZnO-SiO₂/Mt Before Pyridine Adsorption (b) 10ZnO-SiO₂/Mt Before Pyridine Adsorption (c) 5ZnO-SiO₂/Mt After Pyridine Adsorption (d) 10ZnO-SiO₂/Mt After Pyridine Adsorption (e-f) Details of Pyridine-Adsorbed Samples

adsorption-desorption isotherm curves of the samples are appropriate to the type V which could be attributed to relatively weak adsorbent-adsorbate interactions, and particularly, pore filling occurs at high P/P^0 . The hysteresis loop appeared by both 5ZnO-SiO₂/Mt and 10ZnO-SiO₂/Mt is the distinctive feature of the Type H3 loop which is characteristic for a non-rigid aggregate, including plate-like particles of clay minerals. This type is confirmed by the pore size distribution exhibiting the pores dominantly in microporous range (<10 nm).

Table 2. Surface Acidity of Prepared Materials

Sample	L/B	Total acidity (mmol n-butylamine/g)
Mt	1.04	0.78
5ZnO-SiO ₂ /Mt	2.71	1.01
10ZnO-SiO ₂ /Mt	3.98	1.12

The BET specific surface area of the modified samples obtained in this work is lower than were gained by porous clay heterostructure (PCH)-supported ZnO and PCH formation using TEOS (Abou Khalil et al., 2015; Rubiyanto et al., 2020) but it is higher than the exhibited by ZnO-pillared montmorillonite (Bezerra et al., 2025; Hur et al., 2006). The higher specific surface area of modified montmorillonite is usually created by the addition of surfactant as directing agent of metal oxide crystal formation within the interlayer space.

The change in textural properties is confirmed by morphological images of the materials from SEM analysis (Figure 5). The flaky structures are demonstrated by both ZnO-SiO₂/Mt samples, that are rougher compared to the surface of Mt sample. The appearance is similar to was reported by ZnO-modified montmorillonite (Hur et al., 2006). Referred to investigation on textural properties caused by the delamination of the clay layers, the flaky and rougher surface structures discernible from the prepared composites are related to the increased d_{001} identified from XRD analysis (Ramadan and Esawi, 2026). The correlation between d_{001} and textural morphology was identified from TEM investigation on the effect of primary amines-modified montmorillonite (Kashif et al., 2025). In addition, the EDX analysis revealed the inserted zinc oxide as represented by the detectable zinc content of 5.45 %wt. and 12.4 %wt in 5ZnO-SiO₂/Mt and 10ZnO-SiO₂/Mt that are lower than theoretical dispersed amount of 6.5 %wt. and 13.0 %wt, respectively. The filtration and washing processes may cause the leached minerals, especially that are not form the chemical bonding with the montmorillonite structure.

To investigate the bonding in the nanocomposites and also surface acidity, pyridine adsorption followed by FTIR analysis was performed. FTIR spectra of the prepared materials before pyridine adsorption (Figure 6a-6b) show some bands attributed to surface silanol (Si-OH) groups at around 980-990 cm⁻¹ and related absorption identifying the Si-O-Si bonding (Hidayatullah et al., 2025). These peaks are found in either the silica content in the montmorillonite structure or silica modification.

The existence of zinc is identified by peaks around 702 cm⁻¹ ascribed to ZnO-SiO₂ and peaks at less than 500 cm⁻¹, implying Zn-O bonding in both samples. Details on surface acidity are confirmed by peaks ranging from 1400-1600 cm⁻¹. From the compared spectra, it is seen that the pyridine-adsorbed samples (c-d) show appreciable transmittance compared to raw samples (a-b) (before pyridine adsorption). Using a detailed investigation of the samples after pyridine adsorption, there are three regions as indications for the adsorbed Lewis and Brønsted acids, whereas the peaks of adsorbed Brønsted and Lewis acids appeared at 1549cm⁻¹ and 1449 cm⁻¹, respectively. Moreover, the combined adsorbed Brønsted and Lewis sites is identified at 1500 cm⁻¹. Based on the peak areas, 10ZnO-SiO₂/Mt shows higher acidity compared to 5ZnO-SiO₂/Mt, and the Lewis-to-Brønsted acidity ratio is determined by the following equation (Equation 3):

$$L/B : \frac{\text{Absorption at } 1449 \text{ cm}^{-1}}{\text{Absorption at } 1549 \text{ cm}^{-1}} \quad (3)$$

Gives the values of 2.71 and 3.98 for 5ZnO-SiO₂/Mt and 10ZnO-SiO₂/Mt, respectively. This suggests that the more dispersed zinc oxide in the nanocomposite provides more Lewis acid sites to bind with the pyridine Lewis base site. As studied by evaluating Lewis acidity of cation-exchanged montmorillonite, metal cations act as electron pair acceptor in the Lewis acid-base interaction with the electron pair in the nitrogen of the pyridine structure (Shimizu et al., 2008). The surface acidity and L/B ratio determine the activity for acid-catalyzed mechanisms. Total acidity of the samples is listed in Table 2.

Both the total acidity and L/B ratio are increased as the increasing zinc content. The dispersed zinc on the catalyst surface facilitates the adsorption of n-butylamine by either Lewis acid-base interactions or Brønsted acid-base interactions (Inchaurredo and Font, 2022; Nagvenkar et al., 2015; Ponce et al., 2026).

3.2 Catalytic Activity Performance

Catalytic activity of the prepared materials was assessed for citronellal conversion into isopulegol, referring to the mechanism presented in Figure 7. The activity of the prepared material to convert citronellal and produce isopulegol is reflected by the plots presented in Figure 8. At varied time of the reaction; 1- 3 h, the conversion is increased at longer time of reaction, which the conversion values gained by ZnO-SiO₂/Mt samples are higher than that of Mt. The conversion of more than 95% at the time range for ZnO-SiO₂/Mt samples ZnO-SiO₂/Mt samples, meanwhile Mt shows conversion ranging at 32-37%. These conversion values obtained by Mt are within the range reported by previous works (Fatimah et al., 2025, 2015; Rubiyanto et al., 2020). At 3 h, there are about 99.99% of citronellal was converted over 10ZnO-SiO₂/Mt, and it is 98.40% achieved by 5ZnO-SiO₂/Mt. The higher conversion achievable by 10ZnO-SiO₂/Mt rather than that of 5ZnO-SiO₂/Mt suggests that, as hypothesized, the provided surface acidity and surface area are supportively enhancing the

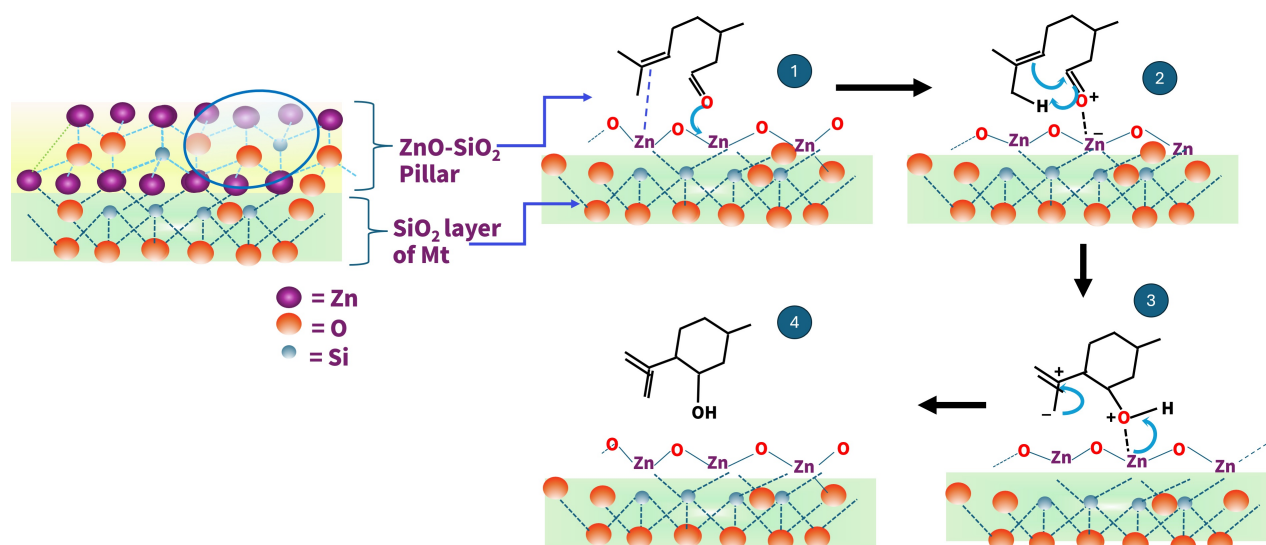


Figure 7. Catalytic Mechanism of Citronellal Conversion into Isopulegol

Table 3. Comparison on Catalytic Activity of Prepared Samples with Previous Works

Catalyst	Reaction condition	Remark (Conversion and selectivity)	Reference
Zeolite-supported Nickel (10% wt.)	Temperature: 200°C, catalyst loading: 0.1 g/10 mL, time: 1 h, No solvent, additional condition: H ₂	C = 100%, S _{iso} = 40%	(Tursiloado et al., 2015)
Sulphated zirconia	Temperature: 78°C, catalyst loading 100 mg/25 mL, solvent: cyclohexane, time: 80 min, additional condition: helium flow	C = 100%, S _{iso} = 90%	(Piña-Victoria et al., 2024)
Zr-pillared montmorillonite	Temperature: 90°C, catalyst loading 200 mg/25 mL, solvent: no solvent, time: 60 min	C = 90.34%, S _{iso} = 5.98%	(Fatimah et al., 2016)
Pt-saponite	Temperature: 90°C, catalyst loading 200 mg/25 mL, solvent: isopropanol, time: 60 min	C = 99.99%, S _{iso} = 14.08%	(Fatimah et al., 2016)
Porous clay heterostructure (SiO ₂ -Montmorillonite)	Temperature: 90°C, catalyst loading 200 mg/25 mL, solvent: isopropanol, time: 60 min	C = 100%, S _{iso} = 22.15%	(Rubiyanto et al., 2020)
ZnO-SiO ₂ /montmorillonite	Temperature: 90°C, catalyst loading 200 mg/25 mL, solvent: isopropanol, time: 180 min	C = 99.99%, S _{iso} = 66.39%	This work

catalytic mechanism (Piña-Victoria et al., 2024). Moreover, the enhanced physicochemical features by the modified Mt exhibit the enhanced S_{iso}. During the reaction time of 1-3 h, 10ZnO-SiO₂/Mt demonstrates the higher S_{iso} compared to 5ZnO-SiO₂/Mt and Mt, which S_{iso} values are appreciably enhanced with reaction time. Although the S_{iso} shows enhancement by the prepared catalyst, the values are still within the range of 55-67%, lower than

was achievable by phosphate and sulphated-zirconia catalysts with more than 95% (Piña-Victoria et al., 2024). The lower S_{iso} is attributed to some identified side products such as isomenthone, menthone, neoisomenthone, hydroxy citronellal, citronellil acetate, β-methyl-4-methylene- cyclohexaneethanol. Based on previous works, the selectivity towards a specific product of citronellal cyclization, including S_{iso} is influenced by some fac-

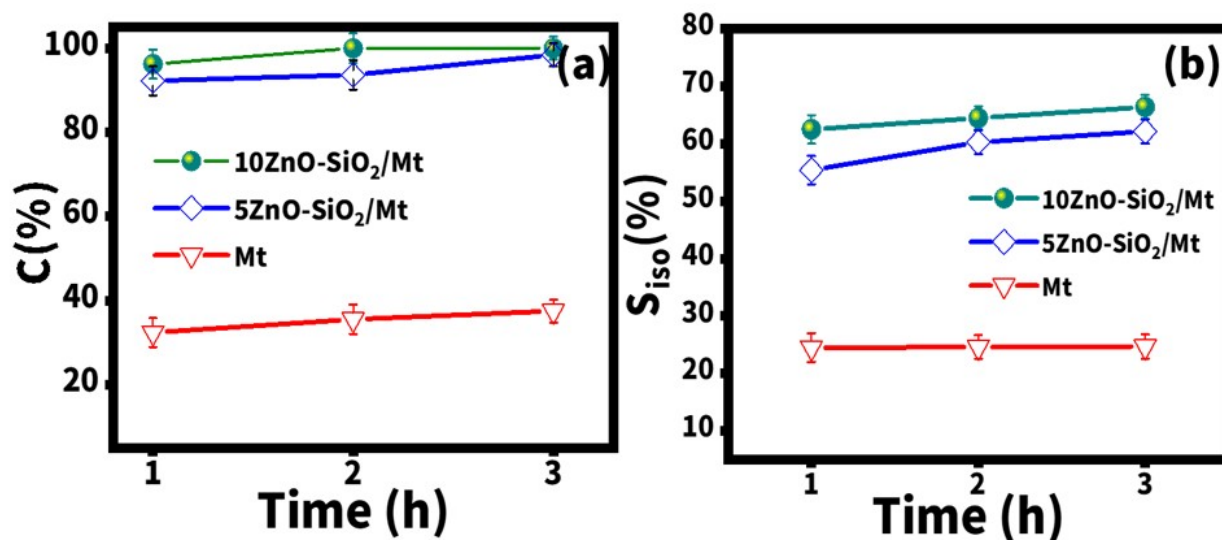


Figure 8. a. Catalytic Conversion, b. Selectivity to Produce Isopulegol as Function of Time Over the Prepared Materials

tors such as surface acidity, acid strength and type, pore size distribution, etc. (Shah et al., 2019). From a study of phosphotungstic acid-modified montmorillonite, the higher acidity and strong Lewis acidic sites affected to increased catalytic activity and selectivity towards isopulegol, meanwhile the porosity of catalyst ineffectively influential. From the use of ZSM-5 catalyst, mesoporosity and pore size distribution that are tunable from desilication treatment play more important role to major changes in conversion and selectivity (Shah et al., 2019). It could be said that in this work, both surface acidity and textural properties influence catalytic activity and selectivity. Table 3 lists the comparison of the catalytic activity with other montmorillonite-based catalysts.

4. CONCLUSIONS

This study presents a microwave-assisted synthesis of bimetal oxide ZnO-SiO₂-pillared montmorillonite focusing on physicochemical characterization and catalytic activity in citronellal conversion into isopulegol. The prepared materials at varied zinc contents of 5 mmol/g and 10 mmol/g demonstrated the significance elevated specific surface area as consequence of the zinc-silica pillars formation in the intra-gallery structure of montmorillonite. The enhanced surface porosity is correlated with the increased surface acidity that supports catalytic activity in citronellal conversion to isopulegol. A conversion of 99.99% and selectivity towards isopulegol of 66.39% were obtained by 10ZnO-SiO₂/montmorillonite at 3 h of reaction time.

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