

Article

Ni Dispersed on Sulfated Zirconia Pillared Montmorillonite as Bifunctional Catalyst in Eco-Friendly Citronellal Conversion

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Abstract. Preparation of nickel dispersed on sulfated zirconia pillared montmorillonite (Ni/S-Zr/MMT) and its application as catalyst in citronellal conversion was investigated. Preparation of material was conducted by three main steps; zirconia pillarization, sulfation and nickel dispersion. The synthesized material was characterized with FTIR spectroscopy, elemental analysis, x-ray diffraction and gas sorption analyzer and catalytic activity was tested for microwave assisted citronellal conversion via catalytic hydrogen transfer mechanism. The results showed that the obtained material gave high total conversion and demonstrated cyclization, isomerization and hydrogenation mechanism in one pot reaction. The presence of sulfate and nickel in the catalyst play important role within the mechanism.

Keywords: Pillared clay, zirconia, nickel, citronellal, cyclization, hydrogenation.

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1. Introduction

Heterogeneous catalyst contributes and plays important role in green chemistry including in organic synthesis. Beside of the regenerable and reusable properties, heterogeneous catalyst can covers and give direction to increase selectivity of certain product designing structure and properties of the catalyst [1]. In the organic synthesis, citronellal can be converted to produce isopulegol and menthol as important compounds in the synthesis of fragrance chemicals. Isomerization, cyclization and hydrogenation mechanisms are required within the process. In previous researches and industrialization, the cyclisation and isomerization of citronellal proceeds readily with various homogeneous catalysts, but the catalyst frequently cannot be recovered and reused [2, 3]. In other case, two-steps reaction is widely performed and lead to a high energy and time consumed process. In order to increase the efficiency of reaction and process, some investigations dealt with developing heterogeneous catalysts with an environmental friendly, reusable and economic features. Metal modified clay materials have been found to be active and demonstrated the contribution to environmental friendly process in some organic reactions by some advantageous of recovery, regenerable and reusable reasons [4]. The catalytic activity can be generated by modification of the silica-alumina framework by elements having Lewis acidity such as Ti and Zr and also sulfation process of the pillared materials [5]. In previous work we have demonstrated the high conversion of citronellal to isopulegol with Ti and Zr pillared clay from montmorillonite clay as raw material also effect of sulfation process to zirconia pillared montmorillonite. Considering the potency of pillared smectite and its sulfated form to preserve catalytic sites, in the present work we extend the applicability of pillared clay materials as support of bifunctional heterogeneous catalysts to produce futher intermediates in a one pot conversion system as called as a tandem cyclization-hydrogenation [2, 3, 6]. A series of bifunctional catalysts based on Ni immobilized S-Zr-pillared clay derived from montmorillonite and saponite as raw clay were prepared. Aims of research are to study the physicochemical character of clay materials by the modificayion and furthermore the relation between the physicochemical characters and the catalytic activity. Reaction conversion, selectivity to a certain product and catalysts reusability were evaluated based on the term of green conversion.

2. Materials and Method

2.1. Materials

Natural montmorillonite powder obtained from PT.Tunas Inti Makmur, Semarang, Indonesia (CEC : 69 meq/100g) was utilized as raw material in material preparation. Chemicals in pro analyst grade consist of $ZrOCl_2 \cdot 8H_2O$, $NiSO_4 \cdot 6H_2O$, $BaSO_4$, pyridine, n-butylamine, citric acid were used without further purification and obtained from standard commercial suppliers (Merck). Meanwhile, instrumentations used in this research were XRD Shimadzu X6000, Nicolet Avatar FTIR instrument, SEM-EDX Seiko, NOVA 1200e gas sorption analyzer.

2.2. Method

Natural montmorillonite was activated by refluxing in sulfuric acid for 6h followed by neutralization and heating before was utilized. Preparation of materials was conducted in three main steps; zirconium dioxide pillarization to obtain zirconia-pillared montmorillonite(Zr/MMT), sulfation of Zr/MMT to produce sulfated zirconia montmorillonite(SZr/MMT) and finally nickel dispersion by impregnation method. The pillarization was engaged by using Zr_4 polyoxocation with zirconium precursor from $ZrOCl_2 \cdot 8H_2O$. Zirconium precursor was made by dilluting $ZrOCl_2 \cdot 8H_2O$ solution with the addition of Ba until the mole ratio of Zr:Ba is equal to 20 and then the solution was aged for a night under stirring. The addition of Ba was aimed to stabilize the formed Zr_4 polyoxocation [7]. The solution was then dispersed into a suspension of montmorillonite in water (5%wt.) with the theoretical Zr content of 20mmol/g. The mixture was stirred for a night before refluxed for 6h. The result was filtrated to get solid and after that the solid was neutralized by the addition of double distilled water until the pH of the filtrate is equal to 7, Cl⁻ ion free and the conductivity is less than 0.01 μ S. Obtained solid that was then dried, grounded and calcined at 400°C for 4 to get zirconium pillared montmorillonite (Zr/MMT).

Sulfation process to Zr-MMT to produce SZr/MMT was referred to as reported in previous investigation on sulfated zirconia preparation. Ammonium sulfate and Zr.MMT with a molar ratio of 1:6 were ground in a mortar for 20 min at room temperature followed by calcination 5 h at 600 °C. Furthermore the impregnation of nickel into Zr/MMT and SZr/MMT was conducted at the theoretic nickel content of 2.0% wt. Precursor solution of Ni from NiSO₄.6H₂O was added into SZr/MMT powder and mixed by stirring. Solvent evaporation was performed to find solid that was then calcined at 400°C for 4h before reduction under H₂ gas at 300°C for 2h. For comparison, nickel dispersion was also performed for Zr/MMT.

All catalyst sample was characterised by XRD, N₂ adsorption at 77K, SEM-EDX analysis and surface acidity measurement based on pyridine adsorption followed by FTIR analysis. For characterization purposes, X-ray diffraction (XRD) patterns were obtained with Rigaku using Ni-filteredCu K α . In order to evaluate Broensted to Lewis acid ratio, Fourier-Transform infrared (FTIR) analysis using pyridine as the probe molecule was used. Spectra of the samples as well as the spectra of pyridine adsorbed on the samples were recorded on a Nicolet Avatar FT-IR spectrometer (Impact 410) with a resolution of 1 cm⁻¹. The samples were placed in an evacuated cell before pyridine adsorption treatment for 24h. After reevacuated for 4h at room temperature the infrared spectra were recorded. Elemental analysis to the samples was analyzed by electron diffraction x-ray (EDX) patterns were recorded on a JEOL 2010 with an acceleration voltage of 200 kV. Surface parameter of BET specific surface area, pore volume and pore radius were determined based on the nitrogen isotherms at 77 K were measured using a Micromeritics ASAP 2010 system.

2.3. Catalytic Activity Test

The catalytic cyclization-hydrogenation reactions were carried out in a batch reactor. Reactions were carried out in a microwave reactor at the frequency of 2469Hz, 100W glass reactor for 15 mins. For each reaction, 0.1g of catalyst was added into the mixture of 10mmol citronellal in 5mL 2-propanol as solvent and 4mmol ammonium formate as catalytic hydrogen transfer agent. Result of reactions were analyzed with a Shimadzu Gas Chromatograph coupled to a mass spectrometer using a HP-5MS capillary column. The reaction conversion was calculated by following formula:

$$\text{Total Conversion} = \frac{\text{initial concentration of citronellal} - \text{Citronellal concentration in product}}{\text{initial concentration of citronellal}} \times 100$$

3. Result and Discussion

Figure 1 shows XRD diffractograms of Zr-MMT and S-Zr/MMT, Ni/Zr-MMT and Ni/S-Zr/MMT catalysts in comparison with activated montmorillonite. The averaged basal spacing (d-spacing) of Na-MMT and each modified MMT were calculated by Bragg's law ($2d\sin\theta = n\lambda$). The results indicate the increasing d001 of montmorillonite structure as shown by the shift of d001 reflection of montmorillonite to the lower angle in Zr-MMT. This shift correspond to insertion of zirconia as bigger molecule compared to native cations between silica-alumina sheets as illustrated by the schematic representation depicted in Fig. 2. This phenomena is similar to that was reported in MMT modification by using ammine molecules [8].

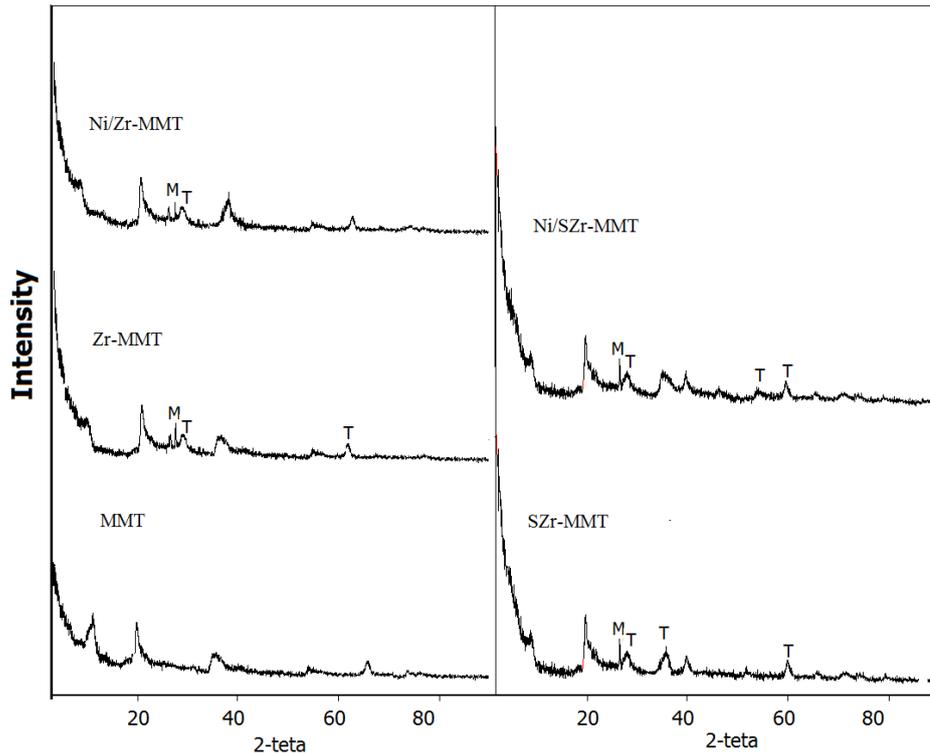


Fig. 1. XRD pattern of prepared materials.

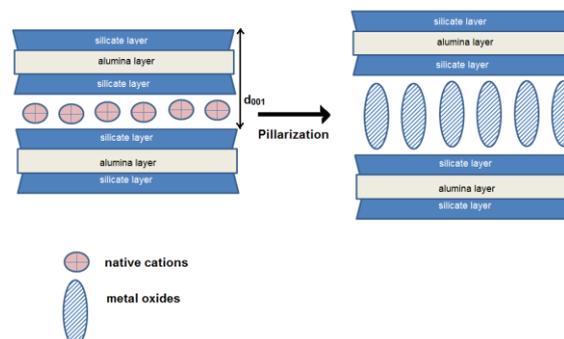


Fig. 2. Schematic representation of MMT pillarization.

From the reflections analysis, it is confirmed that zirconia particles are formed in the pillarization process as shown by reflections at $2\theta = 30.3^\circ$, 35.3° , 50.7° , and 60.6° which are assigned to tetragonal phase and monoclinic phase refer to reflection at $2\theta = 24.7^\circ$. Crystallinity of the tetragonal phase seems to be intensive after the sulfation [5, 9–11].

After sulfation process there is reduction of the crystallinity as shown by wider and lower intensity of d_{001} reflections compared to that of MMT and Zr-MMT. It may related to the stability of zirconia pillar between the layer structure of the montmorillonite. Furthermore nickel impregnation seems give no significant effect to the structure either there is no specific reflection related to the presence of nickel particle appeared. This is possibly come from the low content of nickel as can be seen from the elemental analysis data presented in Table 1 informing that the nickel content is about 2%. The similar result was reported from the nickel dispersion on clay minerals which was no nickel phase identified [12–13].

FTIR spectra of pyridine-adsorbed materials is depicted in Fig. 3. The band at 462cm^{-1} in MMT is correspond to the Si-O-Si and the bands at 1044cm^{-1} and at around 800cm^{-1} are indication for the presence of tetrahedral environment vibration. The bands at around 1636cm^{-1} in all samples are associated to the presence of Si-OH. Compared to raw MMT, those bands that are characteristics for the presence of silica and alumina structure of montmorillonite are shifted into the higher wavenumber after zirconium pillarization and nickel dispersion. This is because the insertion of zirconium and nickel atom contribute to enhance vibration energy of the corresponding bands. It is also found that nickel insertion into the

structure give the absorption at around 668-669 cm^{-1} which associated with Si-O-Ni [12, 14]. As result of pyridine adsorption to the samples, all samples show the spectra characteristic for pyridine. All sample show the absorption band at around 1540 cm^{-1} and 1450 cm^{-1} which correspond to the presence of Broensted and Lewis sites via the interaction between surface and pyridine structure. Effect of sulfation was exhibited by additional band at 1223-1227 cm^{-1} as assigned to typical band for bidentate sulfate coordinated to zirconium cation [15].

Table 1 shows the calculated surface acidity based on n-butylamine adsorption and FTIR spectra by following equation:

$$\text{Broensted to Lewis acid ratio (B/L)} = \frac{\text{Intensity of band at } 1540\text{cm}^{-1}}{\text{ntensity of band at } 1450\text{cm}^{-1}}$$

Zirconia pillarization, sulfation and nickel dispersion contribute to affect total surface acidity as well as B/L ratio. Zirconia formation in the Zr-MMT structure creates Lewis acid sites from the d-orbital availability as acceptor of pair electrones(Lewis base). Beside of this, hydroxylation during the calcination of Zr-interlayered montmorillonite also produces H^+ acts as Broensted acid sites. In advance, the attachment of sulfate ion on zirconia particles after sulfation process is present in two anchoring bonds to ZrO_2 surface consist of S=O group and coordinated $-\text{OH}$ with Zr^{4+} [16]. Those contribute to enhance both Broensted and Lewis acidity. The phenomena is confirmed by data in Table 1 in that the surface acidity of SZr-MMT is higher compared to Zr-MMT and MMT. While the total acidity of S-Zr/MMT and Zr-MMT is higher compared to MMT, there is a significant change in B/L ratio. The formation of Lewis acid sites from zirconia pillarization reduces B/L ratio and after that by sulfation process B/L ratio is going increased. Similar effect with zirconia attachment in MMT structure, the dispersion of nickel exhibits Lewis acid creation due to nickel capability to catch Lewis base so the B/L ratio was then reduced.

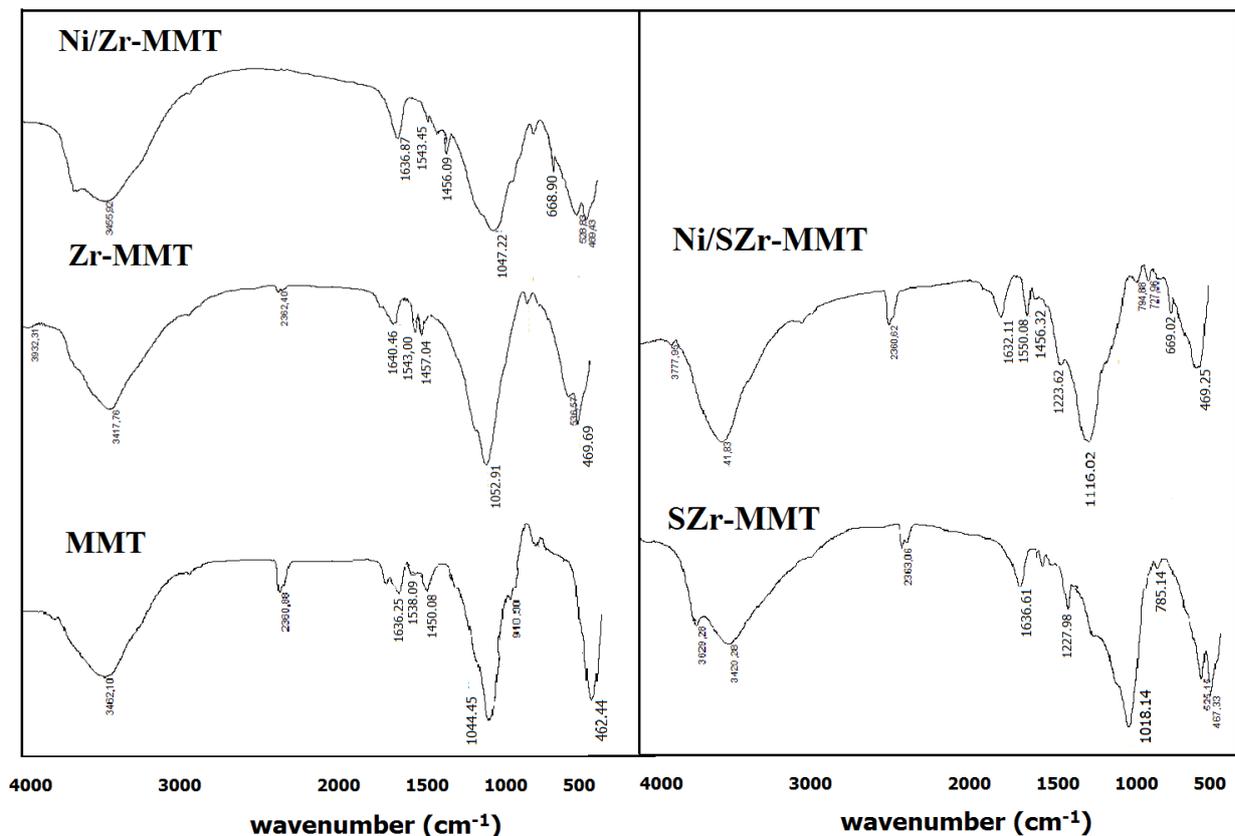


Fig. 3. FTIR spectra of pyridine-adsorbed materials.

Table 1. Total surface acidity and B/L of materials.

Sample	Total acidity (meq n-butylamine/ sample)	B/L
MMT	0.6505	1.12
Zr-MMT	1.4852	1.05
SZr-MMT	1.5570	1.13
Ni/SZr-MMT	1.5580	0.998

Elemental analysis result and the surface parameter consist of Brunair-Emmet-Teller(BET) specific surface area, pore volume and pore radius are presented in Table 2 and Table 3.

Table 2. Result of elemental analysis of materials.

Sample	Element (%wt.)					
	Si	Al	Zr	Mg	Ni	Fe
MMT	17.89	8.98	nd	0.99	nd	3.21
Zr/MMT	17.77	6.65	12.09	0.98	nd	3.11
SZr/MMT	16.89	6.66	11.34	0.87	nd	2.89
Ni-Zr/MMT	15.75	6.05	11.05	0.89	1.80	2.91
Ni-SZr/MMT	15.89	6.16	11.06	0.88	1.78	2,78

From the data in Table 2, it is seen that silica and alumina are major component of MMT because both elements are in the main framework structure of MMT. After was modified by pillarization and further treatment, appreciable reduction of Al content was occurred. This is probably caused by the dealumination that may occurred as the effect of interaction between polyoxocation during the intercalation as well as thermal treatment during the calcination process [17].

Table 3. Surface parameter of materials.

Sample	Surface parameter		
	BET-Specific surface area (m ² /g)	Pore Volume (cc/g)	Pore radius
MMT	69.88	33.4x10 ⁻²	6.78
Zr/MMT	134.55	4.56x10 ⁻¹	7.99
SZr/MMT	198.09	5.66x10 ⁻¹	9.79
Ni-Zr/MMT	13.268	7.9 x 10 ⁻²	11.90
Ni-SZr/MMT	34.557	15.78x10 ⁻²	12.34

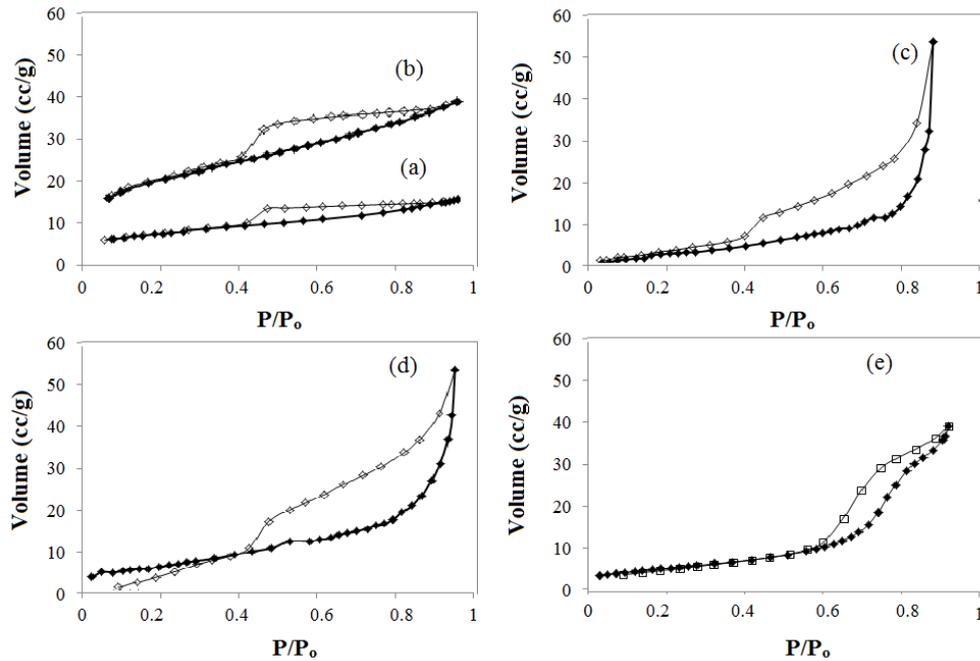


Fig. 4. Adsorption-desorption profile of (a) MMT (b) Zr/MMT (c) SZr/MMT (d) Ni-Zr/MMT (e) Ni-SZr/MMT.

Refer to surface parameter, it can be seen that modification of montmorillonite by zirconia pillarization and sulfation gave higher surface parameter of BET specific surface area and pore volume compared with raw montmorillonite. Adsorption-desorption profiles of the materials in Fig. 4 are also represent the change in type of porous structure in that after sulfation and nickel insertion there are hysteresis loop. The formation of metal oxide pillar and also sulfate attachment in the pillar caused the increasing amount of mesopores within the structure. Furthermore these parameter are decreased after incorporation of nickel even the nickel content is low (1.78-1.80%wt.). Comparison on pore radius distribution in Fig. 5 explain that the nickel insertion change the pore distribution. It is assumed that there is house of cards formation caused by both sulfation and nickel insertion in that the dispersion is not homogeneously distributed. The change in surface morphology is presented in Fig. 6. Rougher surface is shown by Zr/MMT and SZr/MMT and after nickel there is a change in surface morphology.

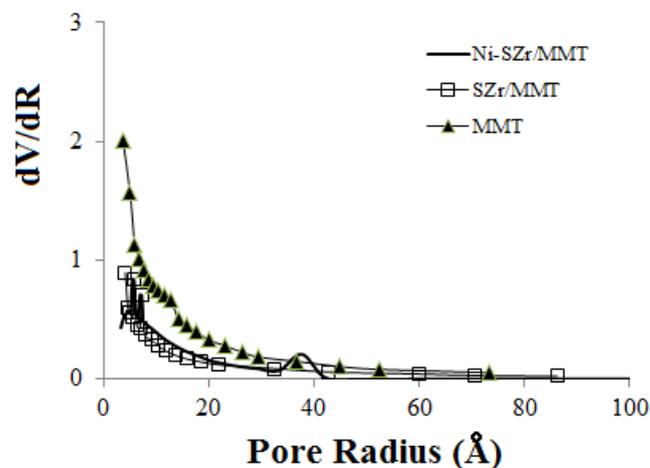


Fig. 5. Pore radius distribution of Ni-SZr/MMT compared with SZr/MMT and MMT.

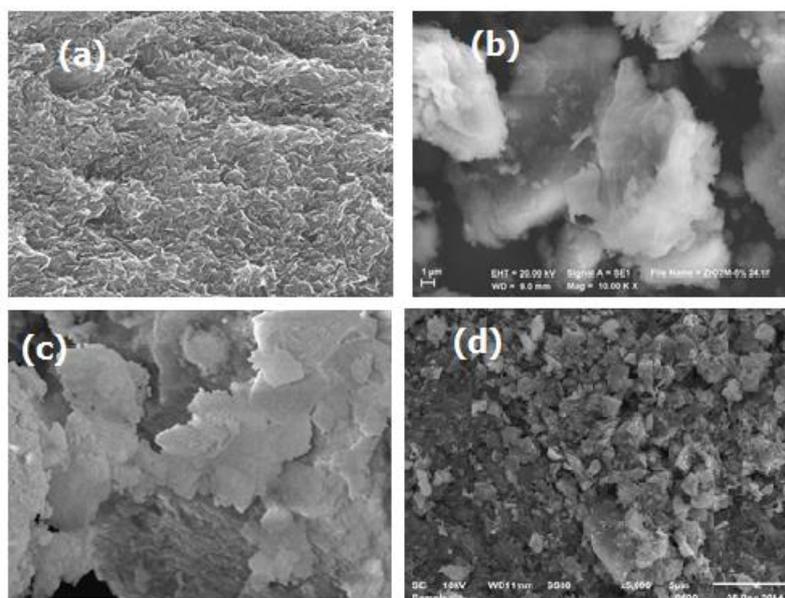


Fig. 6. Surface morphology of (a) MMT (b) Zr/MMT (c) SZr/MMT (d) Ni-SZr/MMT.

Table 4 resumes the parameter of catalytic activity of the materials in microwave assisted conversion of citronellal by catalytic hydrogen transfer mechanism. Catalytic activity are described by total conversion and the selectivity in producing isopulegol, menthol and isomenthone.

Table 4. Catalytic activity parameter of materials.

Catalyst	Conversion(%)	Selectivity to isopulegol	Selectivity to menthol	Selectivity to isomenthone
MMT	68.90	86.78	-	-
Zr-MMT	99.54	100.00	0.00	0.00
SZr-MMT	100.00	92.94	1.51	5.55
Ni/Zr-MMT	100	82.54	4.43	13.03
Ni/SZr-MMT	100	78.09	9.07	12.84

Reaction condition: Microwave frequency: 2469Hz, 15 mins.

Schematic representation of surface mechanism in citronellal conversion to isopulegol, menthol and also isomenthone is described in Fig. 7. Nickel and zirconium atom act as Lewis acid sites contribute to coordinate with double bond and carbonyl group in citronellal molecule and in other scheme sulfate anchored by the surface contribute the Broensted acid so the isopulegol is produced by cyclization mechanism. Furthermore dehydrogenation and hydrogenation may occur on surface to produce isopulegone and menthol products.

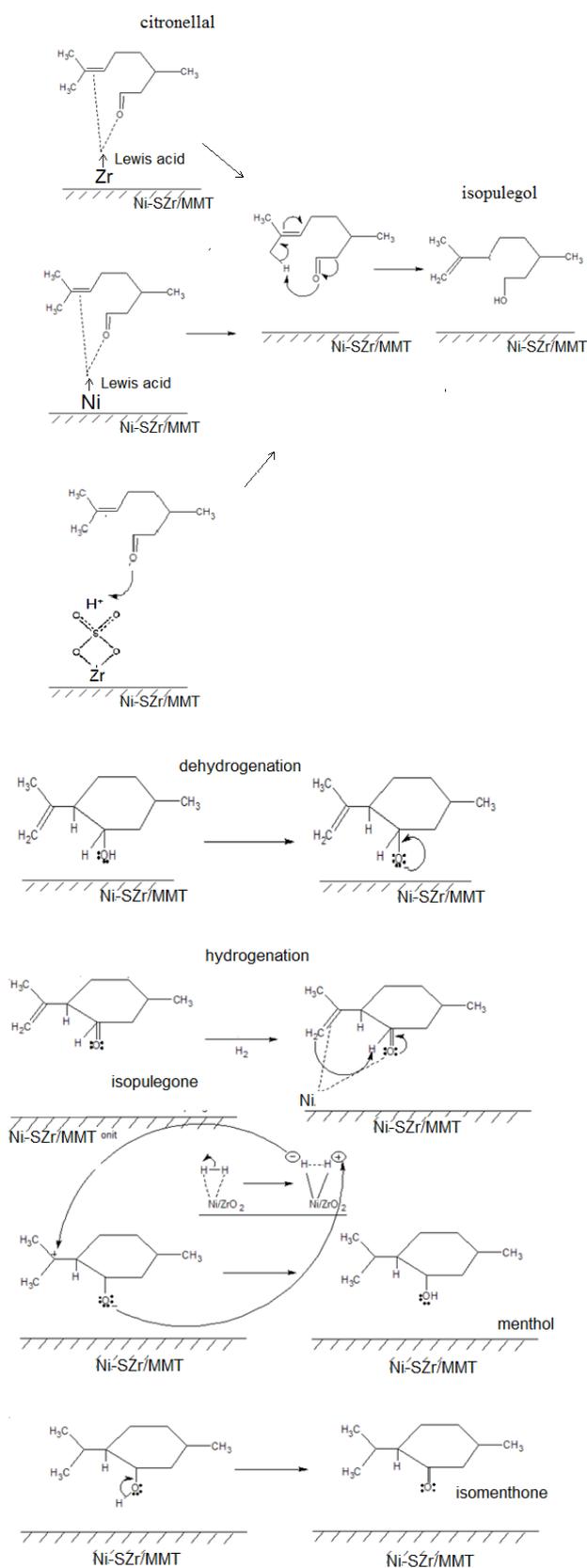


Fig. 7. Surface mechanism of citronellal conversion to isopulegol, menthol and isomenthone.

It was found that modified MMT gives higher catalytic conversion compared to the raw MMT. Important factor that may contribute to the catalytic conversion is related to physicochemical character especially the presence of surface acidity and nickel content in the catalyst. The main product of the conversion over MMT and Zr-MMT is isopulegol as result of isomerization/cyclization mechanism. In advance, the presence of isomenthone which is derived by using SZr/MMT, Ni/Zr-MMT and Ni/SZr-MMT was come from isomerization mechanism of isopulegol. The sufficient surface acidity in the responsible catalysts is main factor in this product. By comparing the selectivity, the isomerization was enhanced by the addition of sulfate ions and furthermore increased by the addition of nickel. Sulfate attachment on zirconium contributes to create both Brønsted and Lewis acid sites on catalyst surface as described by scheme in Fig. 7. Stable acid sites sufficiently accelerate the isomerization via stabilization of cyclization intermediate [18]. Beside of the isomerization, tandem cyclization-hydrogenation over these catalysts were occurred as proven by the presence of menthol. Menthol itself theoretically can be produced by hydrogenation of isopulegol in general or two steps reaction. Although the specific surface area of Ni/Zr-MMT and Ni/SZr-MMT are lower than raw MMT but the presence of sulfate ions and also nickel content activate both cyclization, isomerization and hydrogenation mechanism [19]. The selectivity value in producing menthol of Ni/Zr-MMT and Ni/SZr-MMT are higher compared to S-Zr/MMT suggests that nickel play important role in the hydrogenation mechanism as hydrogen catcher during surface mechanism. The results is in line with some investigation related to hydrogenation mechanism over nickel supported catalyst.

4. Conclusion

Preparation of nickel dispersed on sulfated zirconia pillared montmorillonite has been successfully conducted. From physicochemical characterization it is revealed that there are changes on basal spacing d_{001} of MMT contribute to surface and surface acidity profile of the material. Comparable properties of nickel dispersion on sulfated zirconia-pillared montmorillonite and zirconia-pillared montmorillonite is related to catalytic activity and the selectivity in producing menthol over catalytic hydrogen transfer mechanism.

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