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To cite this article: I. Fatimah, D. Rubiyanto, T. Huda, Z. Zuhrafa, S. P. Yudha & N. C. Kartika (2016): Novel sulphated zirconia pillared clay nanoparticles as catalyst in microwave assisted conversion of citronellal, Materials Technology

To link to this article: <http://dx.doi.org/10.1179/1753555715Y.0000000045>



Published online: 16 Feb 2016.



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Novel sulphated zirconia pillared clay nanoparticles as catalyst in microwave assisted conversion of citronellal

I. Fatimah^{*1}, D. Rubiyanto¹, T. Huda², Z. Zuhrafa¹, S. P. Yudha¹ and N. C. Kartika¹

Preparation of novel sulphated zirconia pillared montmorillonite and saponite clays nanoparticles (SZ/MMT and SZ/SAP) were studied to find a highly active, economist and environment friendly catalysts in the conversion of citronellal into menthol. Sulphated zirconia pillared MMT was prepared by direct sulphation into zirconia pillared MMT, which is a new and fast technique. Comparative study also conducted by evaluating the activity of SZ/MMT with sulphated zirconia nanoparticle (SZ). Material characterisation was performed by X-ray diffraction, Brunauer–Emmett–Teller surface area analysis, scanning electron microscope and also surface acidity by mean pyridine adsorption Fourier transform infrared analysis and total acidity by butylamine titration. Catalytic activity of both SZ/MMT and SZ/SAP was observed in a reaction of citronellal conversion. The operation parameters consist of technique of reaction; tandem cyclisation–hydrogenation and catalytic hydrogen transfer mechanism were investigated. The results show that the pore size of catalyst and the presence of surface acidity affect significantly to increase the isomerisation as well as hydrogenation mechanism. The catalytic hydrogen transfer over microwave irradiation was observed as the more efficient process compared to the tandem cyclisation–hydrogenation from the selectivity of the product and also the other factor influencing the surface mechanism. In another aspect, the results clearly indicated the reusable properties of the sulphated zirconia pillared clay catalysts under varied conditions. Correlation between physicochemical characters and the reaction mechanism is discussed in this study.

Keywords: Pillared clay, Sulphated zirconia, Citronellal, Tandem cyclisation–hydrogenation

Introduction

Recently, environment friendly organic synthesis becomes an interesting technology referring to the principle of green chemistry. Some principles such as minimising chemical, reducing the step of the chemical synthesis and production and consideration on chemical reusability are important efforts by not only researchers but also the industry. For these goals, some investigations were aimed to substitute the use of homogeneous catalyst with heterogeneous catalyst for the organic synthesis, and these are widely investigated. For minimising energy involved within the process, such efficient process like microwave assisted reaction, sonocatalysed reaction, etc. are also interesting and developing techniques.¹ Especially in acid catalysed organic synthesis, heterogeneous catalyst gives some advantages such as its reusability, easy product separation and ability to replace corrosive, hazardous and polluting liquid acids. Solid acid catalysts, both metal oxide

and supported metal oxide leading to better selectivity, have been extensively studied.²

Citronellal conversion to more valuable chemicals is an important reaction in some industries such as menthol, isopulegol and other food flavour and medicine industries. The popular step is the conversion of citronellal to menthol due to the high demand of menthol.^{3,4} The conversion requires acid catalyst within two steps of reaction, i.e. cyclisation and hydrogenation, which can be conducted by both separated and combined process. With green chemistry reasons, for this process, some previous researches tried to enhance the effectiveness of the reaction such as promoting the use of solid acid catalyst, utilising microwave irradiation and also combining these steps into one simple step called tandem cyclisation–hydrogenation and catalytic hydrogen transfer.^{4–6} Examples include a tandem cyclisation–hydrogenation of citronellal over ZnBr₂ catalyst, the use of TiO₂–SiO₂ as heterogeneous catalyst, the use of zirconium pillared clay catalyst and the use of sulphated zirconia catalyst. The processes depend on the activity, selectivity and acidity of the catalyst used. Zirconium oxide is an active catalyst for many reactions, whose surface possesses four chemical properties: acidic, basic, reducing and oxidising. It has become well established that the performance of a heterogeneous catalyst depends not only on

¹Chemistry Department, Islamic University of Indonesia, Kampus Terpadu Universitas Islam Indonesia, Jl. Kaliurang Km 14, Sleman, Yogyakarta 55581, Indonesia

²Professional Program of Chemical Analyst, Islamic University of Indonesia, Kampus Terpadu Universitas Islam Indonesia, Jl. Kaliurang Km 14, Sleman, Yogyakarta 55581, Indonesia

*Corresponding author, email isfatimah@uii.ac.id

the intrinsic catalytic activity of its components but also on its texture and stability.²

As was reported from the use of sulphated zirconia and zirconium pillared clay catalysis within the mechanism, to use sulphated zirconium pillared clay as catalyst is the interesting idea. The presence of Brønsted and Lewis acidity of the clay created by pillarisation and its combination with sulphation is hypothesised to enhance the activity in the catalytic hydrogen transfer mechanism.¹ Referring to these backgrounds, this research is aimed to prepare sulphated zirconium pillared clay and to evaluate its activity in the conversion of citronellal by both tandem cyclisation and catalytic hydrogen transfer reactions. Sulphated zirconium pillared clay was obtained using natural montmorillonite (MMT) and synthetic saponite as raw materials that performed by the pillarisation and sulphation procedures. Physicochemical characterisation of material was evaluated by measuring X-ray diffraction (XRD), gas sorption analysis and also surface acidity measurement based on pyridine Fourier transform infrared (FTIR). Motivated by our ongoing endeavours in the development of an ecofriendly benign catalyst for organic synthesis, this research also studies the comparison of catalytic activity in conventional tandem cyclisation and microwave assisted reaction. The correlation between physicochemical character and catalytic activity in the conversion was focused.

Materials and method

Before its use as heterogeneous catalyst for citronellal conversion, the components of raw clay of MMT and saponite, zirconium pillared clays and sulphated zirconium clays were characterised using XRD, SEM-EDX and specific surface area analysis.

In this investigation, raw MMT was purified by refluxing in 0.1M H₂SO₄ before using. Zirconia pillarisation was conducted by several steps:

- (i) preparation of zirconium pillaring solution by diluting zirconium isopropoxide as zirconium precursor in isopropanol solution
- (ii) dispersion of zirconium precursor into 5% clay suspension in water followed by reflux for 6h
- (iii) filtration, drying and calcination at 500°C for 5h.

The obtained materials by these steps are called Zr/MMT and Zr/SAP for MMT and saponite raw materials respectively. Sulphation process toward Zr/MMT and Zr/SAP was conducted according to a previous method.⁷ The process was conducted by mixing the materials with NH₄SO₄ at the mole ratio of SO₄/Zr of 5:1, by grounding homogeneously in carnelian mortar for 10min followed by heating the solid mixture at 300°C for 3h. The products of the sulphation process are sulphated zirconium pillared MMT and sulphated zirconium pillared saponite and, for further discussion, were coded as S-Zr/MMT and S-Zr/SAP respectively.

Characterisation of materials

Powder XRD patterns of raw and prepared materials were recorded with a powder diffractometer (Philips) using Cu K_α

radiation ($\lambda = 1.54056 \text{ \AA}$) in the 2θ range from 2 to 80° and the step size of 10° min⁻¹. Analysis of SiO₂ and Al₂O₃ was conducted using gravimetric analysis, and for S and Zr, EDX analysis was utilised by means of SEIKO. N₂ physisorption at 77K using NOVA 1200e (Quantachrome, USA) was applied to characterise the Brunauer–Emmett–Teller (BET) surface area and the texture properties, namely, total pore volume V_p and pore diameter D_p , of various investigated solid catalysts. Analysis of surface acidity was performed using pyridine adsorption followed by FTIR investigation to the solids. Fourier transform infrared spectra were recorded in the range of 550–4000cm⁻¹ on an Nicolet AVATAR FTIR spectrometer. From the resulting FTIR spectral pattern, the Brønsted/Lewis acid ratio was analysed based on the intensity of spectra at ~1450 and 1540cm⁻¹.

Conventional cyclisation and tandem cyclisation–hydrogenation reaction (Conv.)

Cyclisation reactions of citronellal conversion were performed in a three-neck flask with a condenser. The reactants in the flask was heated in a heating jacket. In a typical experiment, 0.2mol citronellal was mixed with 2mol isopropanol with the addition of 0.05g catalyst. All reactions were set up at the temperature of 80°C for 3h. The products of the reactions were analysed using a gas chromatograph/mass spectrometer (Shimadzu). For the tandem cyclisation–hydrogenation reactions, a flow reaction system was used. The assembly was similar with the assembly for citronellal cyclisation with a hydrogen septum added. Hydrogen at the pressure of 2kPa was added to the reaction system.

Microwave assisted cyclisation and tandem cyclisation–hydrogenation reaction (MW)

Microwave assisted reactions of citronellal conversion were performed in a microwave oven at the frequency of 2459GHz. A similar mixture with that for conventional cyclisation was filled into a Teflon flask before being heated in a microwave oven for 10min. Different with those of cyclisation, tandem cyclisation–hydrogenation reactions were conducted in a catalytic hydrogen transfer mechanism. Ammonium formate was added to the citronellal and isopropanol mixture. In this scheme, ammonium formate acts as hydrogen donor for the hydrogenation section.⁸

Results and discussion

Elemental analysis to the materials measured using gravimetric (for SiO₂ and Al₂O₃) and EDX is listed in Table 1.

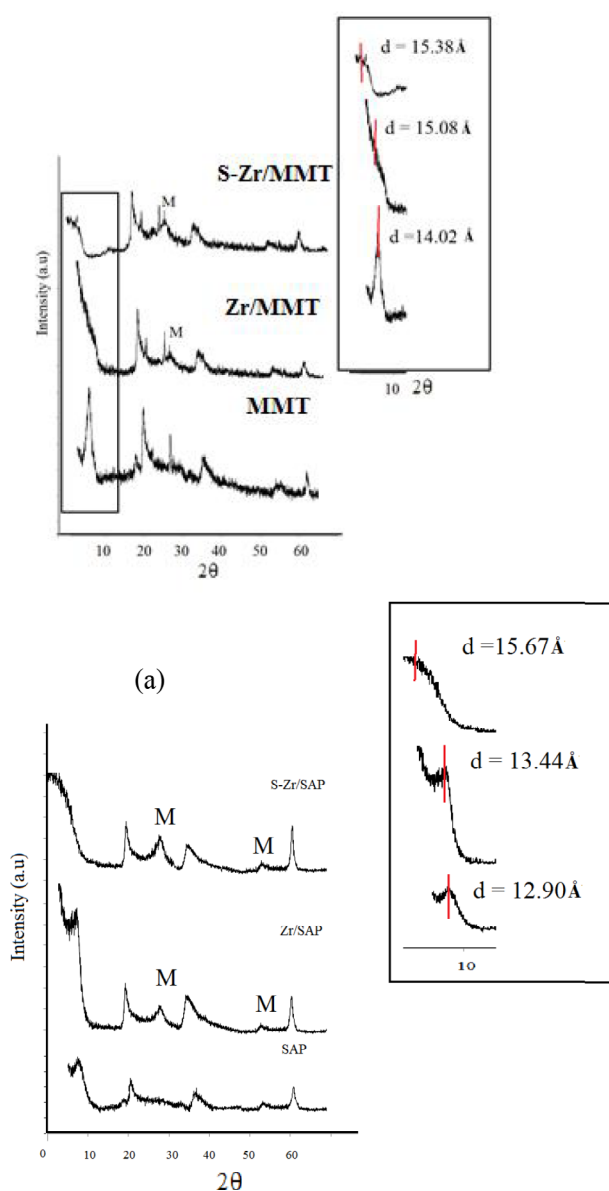
As shown in Table 1, the major contents of raw and modified MMTs are mainly SiO₂ and Al₂O₃, while for saponite and

Table 1 Elemental analysis of materials

Material	SiO ₂	Al ₂ O ₃	MgO	ZrO ₂	S	CEC/ meq/100g
SAP	58.97	6.39	30.88	n.d.	n.d.	99
Zr/SAP	58.9	5.54	26.59	5.09	n.d.	65
S-Zr-SAP	12.44	1.94	10.07	5.19	2.46	66
MMT	59.80	21.9	2.82	n.d.	n.d.	69
Zr/MMT	51.89	18.08	1.78	n.d.	n.d.	45
S-Zr/ MMT	54.29	15.93	1.54	5.07	2.33	47

its pillared and sulphated pillared form are. It is well known that both constituents are the main component of tetrahedral silica and octahedral alumina that build the 2:1 layer structure of MMT as smectite group of clay. Zirconium pillarisation adds the ZrO_2 content of around 5.09-5.19%wt. correspond to the Zr content of about 5%wt. The amounts fit enough to the theoretical content of Zr isopropoxide added in the pillarisation process because of filtration and washing process as sol-gel of zirconium dioxide.

Figure 1 shows the XRD patterns of zirconium pillared clays (Zr/MMT and Zr/SAP) and also its sulphated forms (S-Zr/MMT and S-Zr/SAP). Reflections at $\sim 5.9^\circ$ (001) in all samples indicate the presence of MMT and saponite structure. Indexing of the diffraction peaks was performed using standard Joint Committee on Powder Diffraction Standards file nos. 12-131 and 29-1491 for MMT and SAP respectively. Compared to raw materials of MMT and saponite, Zr/MMT and Zr/SAP showed the (001) reflections at lower angle as a result of the increasing basal spacing d_{001} of smectite clay structure. These observations established the fact of successful intercalation of zirconium oxide into the interlayer space



1 X-ray diffraction pattern of MMT and modified form (M: monoclinic phase of ZrO_2)

of MMT and SAP. The basal spacing d_{001} of MMT increases from 14.02 to 15.08 Å, while for saponite, it increases from 12.90 to 13.44 Å. Another important to be noticed is the formation of new reflections regarding the formation of zirconium oxide in combination of amorph and monocline phases, while the tetragonal phase was not found for both Zr/MMT and Zr/SAP. The formation of the phases is related to thermal transformation of zirconium oxide from its zirconium precursor. Amorphous zirconia can be formed in lower temperature, and it will be slowly transformed into monocline and tetrahedral phases as the calcination temperature increases. Specific reflections that indicate the presence of monoclinic phase are the peaks at $2\theta = 28.38$ and 57.44 (Joint Committee on Powder Diffraction Standards no. 37-1484).^{9,10} The patterns show that sulphation process to zirconium pillared clay does not affect significantly the crystallinity of MMT and saponite minerals, but it seems to increase the formation of monoclinic zirconia in saponite support.

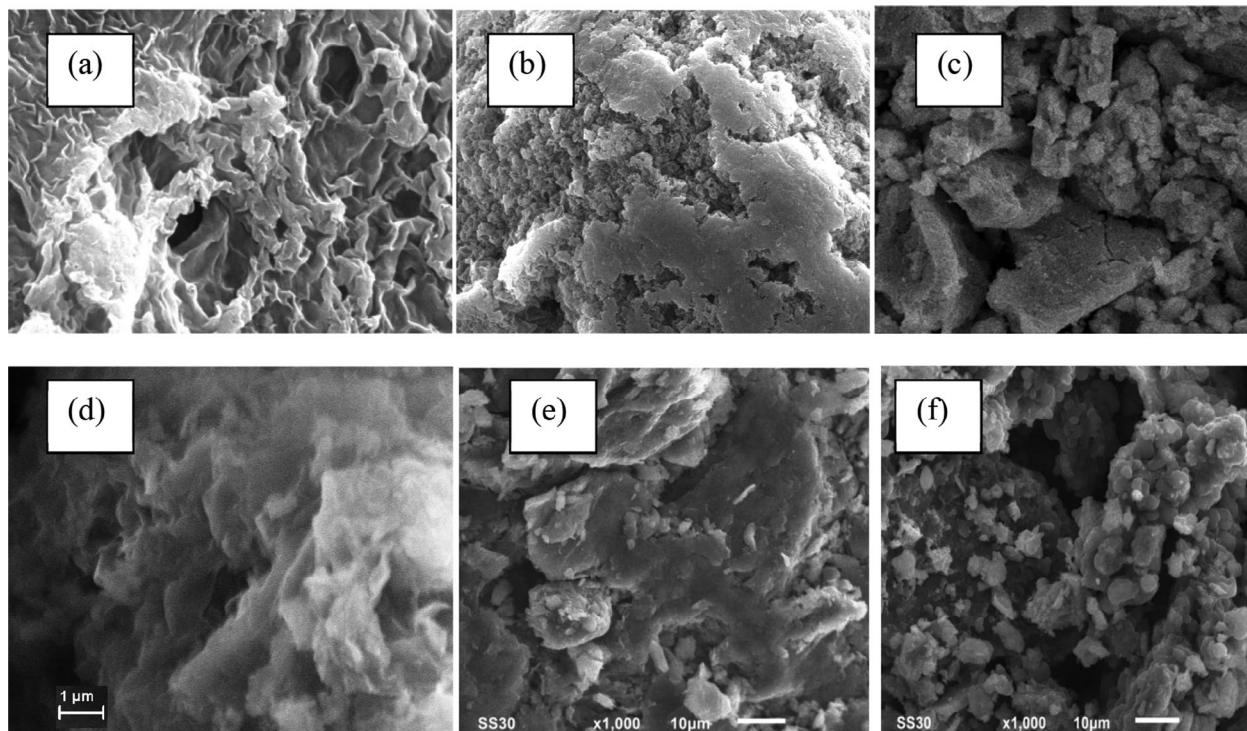
The particle morphology obtained by SEM is compared in Fig. 2. Raw saponite and raw MMT samples show the layer structure morphologies, and then, after the zirconium pillarisation, the surfaces seem to be changed into flaky morphology with random orientation. Insertion of small ZrO_2 particles on the clay mineral particles that are observed by XRD gives such a rougher appearance, which was attributed to the effect of sulphation that opens the surface pores. These comparisons are in line with the surface parameter data, which revealed that sulphated samples have higher specific surface area and pore volume. Some aggregates distributed homogeneously on S-Zr/SAP indicate the formation of higher zirconia crystalline. Surface profile data based on the nitrogen adsorption-desorption in Fig. 3 are presented in Table 2.

The nitrogen adsorption-desorption isotherms of the Zr/MMT and Zr/SAP samples and its sulphated forms are shown in Fig. 2. The filling of a monolayer at relatively low pressures followed by build-up of multilayers until capillary condensation sets in illustrates a typical monolayer and multilayer adsorption on solids with a heterogeneous surface, predominantly macro- and mesoporous structures. According to the International Union of Pure and Applied Chemistry classification, the isotherm corresponds to the type II isotherm for mesoporous materials. The surface profile data of specific surface area, pore volume and pore radius from calculated isotherm data are listed in Table 2.

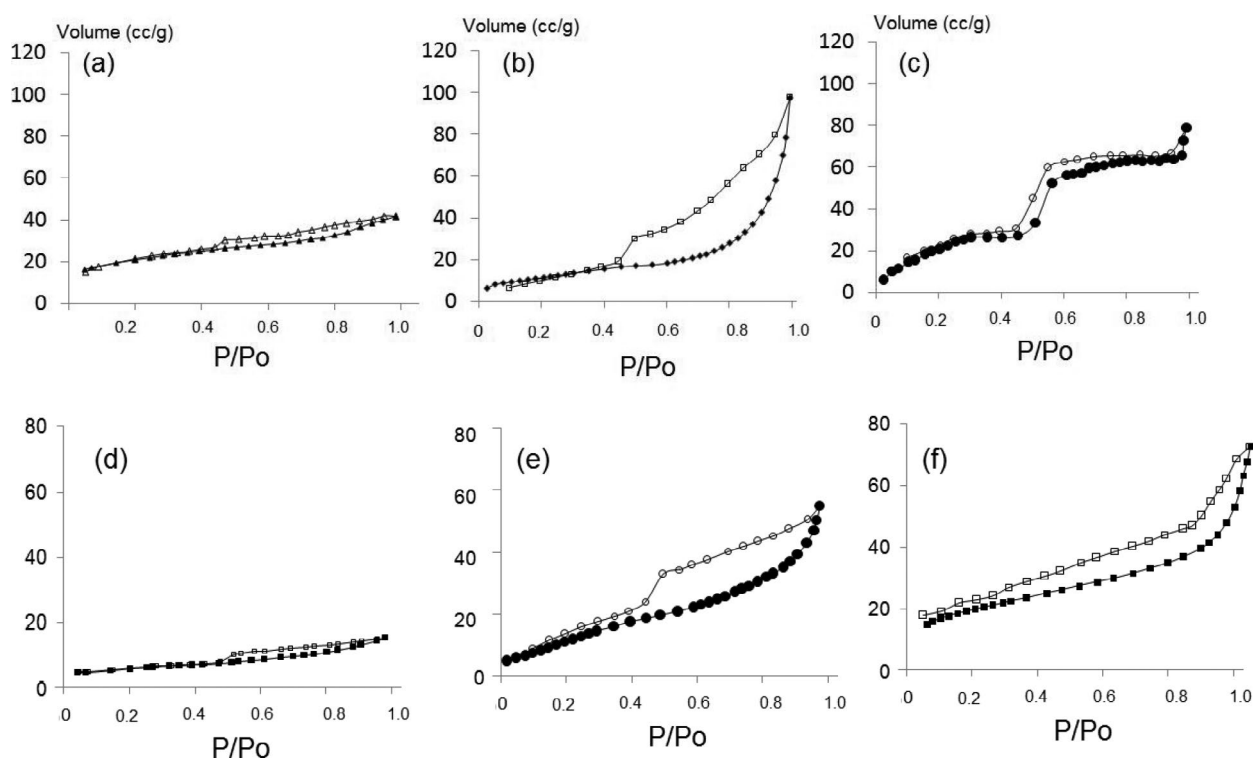
The data support the observation of isotherms that show a significant increase in the BET surface area and pore volume of pillared MMT and sulphated form samples compared with the starting material. Surface area and pore volume of both MMT and SAP were elevated after pillarisation process. It related to the formation of zirconium oxide pillar as confirmed by the shift of d_{001} data from XRD analysis. The BET specific surface area of both Zr/MMT and Zr/SAP were then increased by sulphation procedure. The increasing parameters in zirconium pillared clay are related to the formation of

Table 2 Specific surface area, pore volume and pore radius of materials

Sample	BET specific surface area/ $m^2 g^{-1}$	Pore volume $/ \times 10^{-3} cc g^{-1}$	Pore radius/ \AA
MMT	45.90	1.530	10.70
Zr/MMT	88.99	2.200	11.98
S-Zr/MMT	287.11	0.374	9.30
SAP	123.09	2.370	12.00
Zr/SAP	176.79	5.370	11.09
S-Zr/SAP	189.98	1.589	9.45



2 Profile (SEM) of a MMT, b Zr/MMT, c S-Zr/MMT, d SAP, e Zr/SAP and f S-Zr/SAP



3 Nitrogen adsorption-desorption profile of a MMT, b Zr/MMT, c S-Zr/MMT, d SAP, e Zr/SAP and f S-Zr/SAP

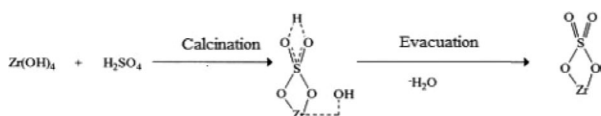
interlayer space, while for sulphated forms, the enhancement of surface profile was caused by pore opening and rearrangement of some micropores in the acid condition from the interaction with ammonium sulphate. According to the XRD data, it is revealed that interlayer structure was maintained even when the surface profile changed. However from pore volume data, it can be seen that decreasing pore volume

occurred after sulphation. From the adsorption-desorption profile presented in Fig. 3, it is noted that there was an evolution of the porous profile. Reduction of pore volume along increasing specific surface area after sulphation indicates that there was formation of aggregates on the surface.

The surface area of the samples increased with the pillariation treatment and further increased by sulphation process.

The increasing specific surface area is in correlation with increasing pore volume. The higher value of both specific surface area and pore volume parameters along with the sulphation due to stabilisation of pores by SO_4^{2-} species. From the result, it can be noted that the specific surface area of all Zr/MMT samples was increased after the sulphation. According to previous investigation, sulphate gives effect to impart a special stabilisation to the catalytically active tetragonal phase of zirconia, which decreases the crystallite size and, consequently, increases the specific surface area, as shown in the following mechanism (1)^{9,12}

Pore evolution in the catalyst materials were consistent with the surface acidity data. Fourier transform infrared spectra of materials are presented in Fig.4.



To measure the acidity, a pyridine adsorption followed by FTIR measurement to the adsorbed sample was performed. The adsorbed pyridine represents the interaction between both Lewis and Brönsted acidity in that the pyridine structure contained aromatic ring and nitrogen with lone pair electrons. Brönsted acidity interaction comes from the aromatic ring and surface, while Lewis acidity is produced from the interaction between nitrogen and metal orbital formed by the aromatic ring. The ratio of Lewis to Brönsted acid is measured by the ratio of the intensity of the spectra at 1560cm^{-1} , which refers to the aromatic chain, to the intensity of the absorption spectrum at 1450cm^{-1} , which is attributed to nitrogen by the following formula

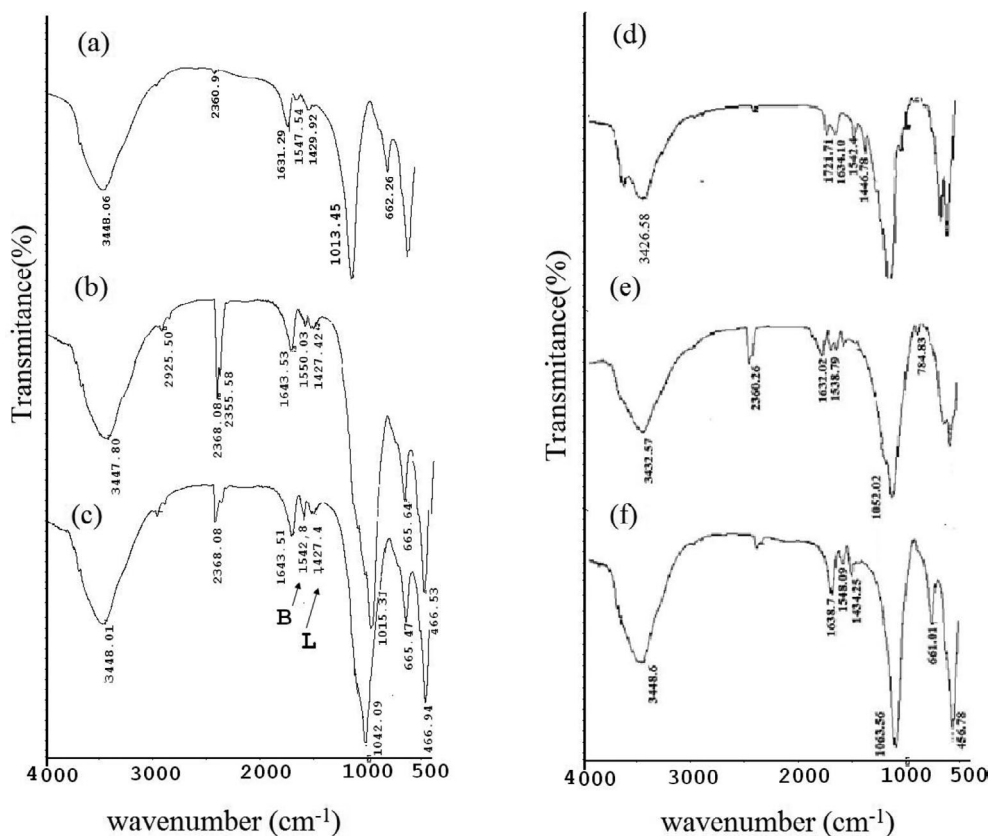
$$\frac{B}{L} = \frac{I_{1540-1560\text{cm}^{-1}}}{I_{1450-1455\text{cm}^{-1}}}$$

The spectra are depicted in Fig.4, and quantitative data from the FTIR spectra and *n*-butylamine titration are tabulated in Table 3. Beside the Brönsted/Lewis acid ratio, the amount of total surface acidity of all solid samples was also measured. The value was calculated based on the adsorbed *n*-butylamine using *n*-butylamine back titration method.

After the pyridine adsorption, all samples show the band at 1540cm^{-1} , which refers the presence of the pyridinium ion, and also absorption at $\sim 1427\text{cm}^{-1}$, which relates to the interaction between acid sites of solid and nitrogen of pyridine. Evaluation on *L/B* ratio showed that zirconium pillarisation increases the ratio and then furthermore was increased by the sulphation. It should be noted that all the pillared materials exhibited a higher total acidity and *L/B* ratio than MMT. Further observation indicated that sulphated materials have higher value of both total acidity and *B/L* ratio compared to its corresponding pillared materials. According to the above facts, there are two factors resulting in the increased surface acidity; the first is the attachment of zirconium dioxide into the interlayer space of MMT structure, and the second is the presence of sulphate functional group that contributes to make an active interaction towards pyridine as probe molecule.

The presence of zirconium, and also the sulphate, on the surface theoretically improves the surface acidity. Brönsted and Lewis acid can be induced and generated by the structure of silica supported metal that is represented by Fig.5.

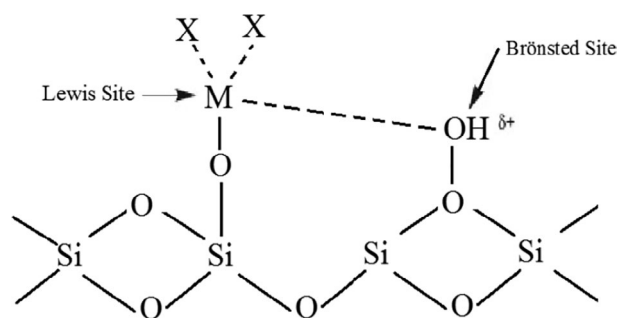
The incorporation of the sulphate anions on the surface of ZrO_2 has been found to probably increase the number and strength of the Brönsted acid sites.



4 Fourier transform infrared spectra of a SAP, b Zr/SAP, c S-Zr/SAP, d MMT, e Zr/MMT and f S-Zr/MMT after pyridine adsorption

Table 3 Total acidity and L/B ratio of materials

Sample	Total acidity/mmol n-butylamine/g	Brönsted/Lewis acid ratio (FTIR)
MMT	0.775	0.85
Zr/MMT	1.075	0.98
S-Zr/MMT	1.120	1.12
SAP	1.108	1.11
Zr/SAP	1.150	1.14
S-Zr/SAP	1.180	1.21

**5 Schematic representation of generating Brönsted acidity from zirconia sulphation**

Furthermore, the correlation between the physicochemical character of materials as catalyst in citronellal conversion was evaluated. The reaction was conducted by both Conv. and MW method, and from each experiment, the product was analysed using gas chromatography/mass spectrometry instrument. The catalyst activity of each catalyst was determined by the parameter of total conversion (%) and selectivity parameters (%) as shown in the following equations (2)–(4)

$$\text{Total conversion} = \frac{[\text{citronellal}]_0 - [\text{citronellal}]_{\text{product}}}{[\text{citronellal}]_0} \times 100\%$$

$$\text{Selectivity}_{\text{product} - i} = \frac{[\text{product}]_i}{\sum_i [\text{product}]} \times 100\%$$

where $[\text{citronellal}]_0$ and $[\text{citronellal}]_{\text{product}}$ are the concentrations of citronellal in unreacted and in the product, $[\text{product}]_i$ is the concentration of a specified product and $\sum_i [\text{product}]$ is the total concentration of all products.

From the data presented in Table 4, it can be concluded that all pillared and sulphated materials demonstrate the higher

catalytic activity as shown by the total conversion value. The total conversion represents the amount of reactant (citronellal) that converted into other products in reaction. The higher total conversion means that interaction between citronellal and catalyst surface can produce other compounds as a product. The more effective interaction between catalyst surface comes from the role of metal oxide in reactant adsorption that is involved in the surface mechanism. Conversion of citronellal can be represented as in Fig. 6.

From the comparison among MMT and saponite raw material, the Zr/SAP gave better conversion and selectivity in terms of both conventional and microwave irradiation method, with almost 100% citronellal was converted to the products, while for Zr/MMT, only 65.78% and 45.67% of citronellal were converted. Generally, the modification to both clay enhanced the catalytic activity by increasing total conversion as well as selectivity to isopulegol product. The catalytic activity of raw MMT and raw saponite comes from the contribution of specific surface area and surface acidity. From compared data, it can be noted that the contribution of specific surface area and the higher surface acidity to the reaction rate is probably the main reason for this phenomenon.¹⁵

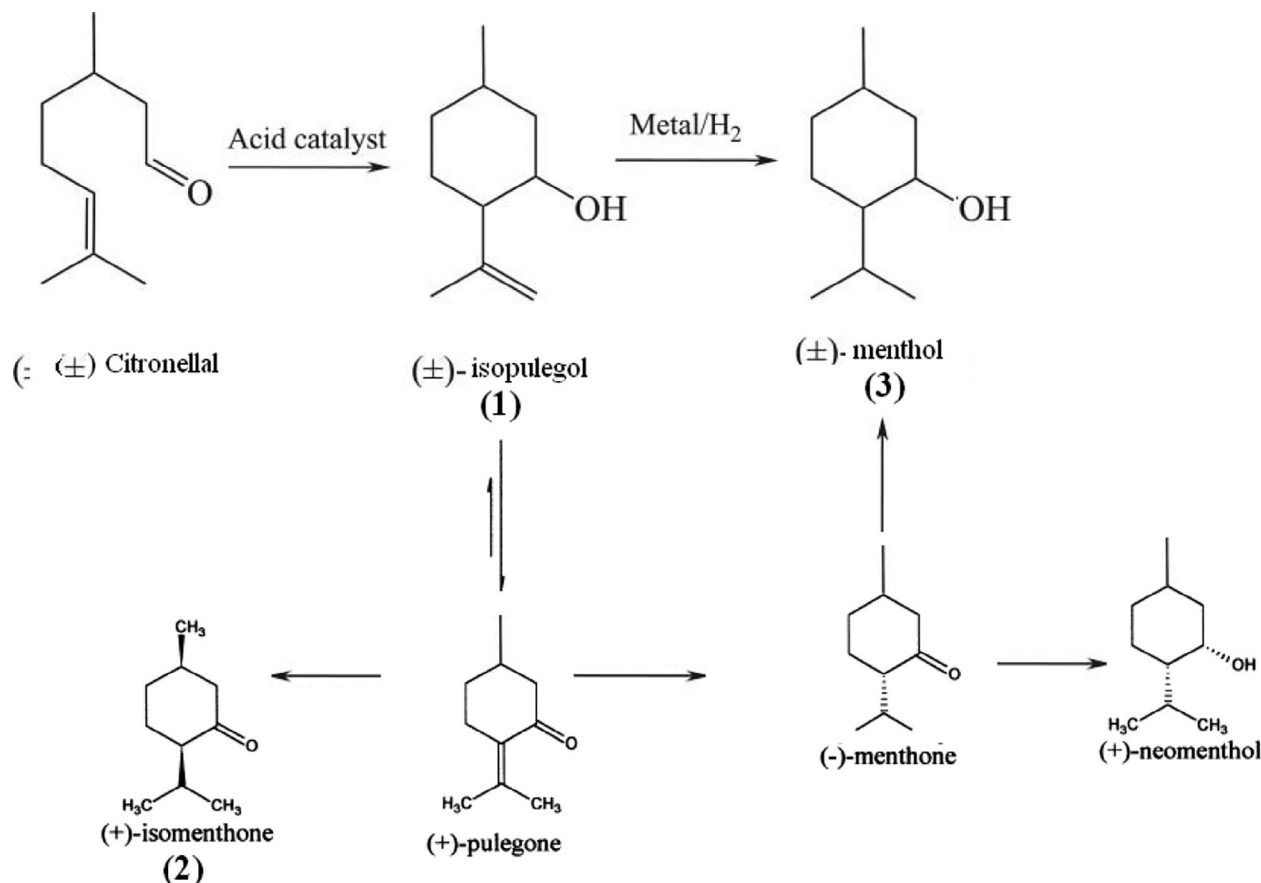
Sulphation procedure to the pillared materials also gave a similar trend in total conversion. Interesting results can be seen from reaction catalysed by the sulphated materials in that other products, except isopulegol, were obtained, e.g. isomenthone and menthol. It is also noted that the higher selectivity towards both compounds was achieved using microwave irradiation method. The catalytic hydrogen transfer mechanism is involved within the conversion. The use of reagents such as ammonium formate is frequently used with environmental benign consideration, and it can be improved by microwave assisted technique. The ability of ammonium format to produce hydrogen was simultaneously collaborated with the ability of hydrogen transfer of zirconium oxide as active metal. However, the hydrogenation mechanism is still low since the selectivity to produce menthol is around 0.98–5.6%.

Conclusions

Catalysts based on sulphated zirconia pillared on MMT and saponite materials were prepared and successfully tested for citronellal conversion. Physicochemical character of the materials revealed that there were some character enhancements regarding the application as solid acid catalyst such as increasing specific surface area as well as solid acidity after zirconia pillarisation and moreover after sulphation process. These characters are in linear correlation with increasing catalytic activity. Catalyst testing shows that

Table 4 Total conversion of selectivity in catalytic testing

Catalyst	Method	Total conversion/%	Selectivity		
			(1)	(2)	(3)
MMT	Conv.	25.48	100
	MW	48.77	100
Zr/MMT	Conv.	65.78	98.6	1.2	...
	MW	45.67	98.56	0.98	...
S-Zr/MMT	Conv.	85.08	96.60	0.21	3.32
	MW	92.29	92.54	0.25	5.6
SAP	Conv.	56.4	100
	MW	80.70	100
Zr/SAP	Conv.	100	100
	MW	100	100
S-Zr/SAP	Conv.	100	95.5	2.0	2.5
	MW	100	30.9	68.0	...



6 Conversion route of citronellal^{13–15}

microwave assisted reaction demonstrated the higher total conversion, while selectivity parameter indicates that the side product of isomenthone was obtained from zirconia pillared materials and in the addition of menthol as sulphation treatment to zirconia pillared materials. The sufficient surface area and metal active sites in sulphated zirconia pillared materials initiated the tandem cyclisation–hydrogenation mechanism.

Acknowledgement

We acknowledge DP2M-DIKTI, Ministry of Education, Republic of Indonesia for Research funding through Hibah Unggulan Perguruan Tinggi with contract no. 0 Hibah Unggulan Perguruan Tinggi with Contract No:060/ Rek/DPPM/UPTL-DIKTI/III/2015.

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