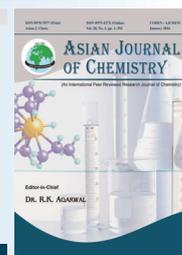




Asian Journal of Chemistry; Vol. 28, No. 11 (2016), 2365-2370

ASIAN JOURNAL OF CHEMISTRY

<http://dx.doi.org/10.14233/ajchem.2016.19879>



Effect of Pt on Catalytic Activity of Al- and Zr-Pillared Smectite

IS FATIMAH*, SEPTIAN P. YUDHA, HAPPY BUNGA N.S., RODHOTUL ULYA and DWIARSO RUBIYANTO

Chemistry Department, Islamic University of Indonesia, Kampus Terpadu UII, Jl. Kaliurang Km 14, Sleman, Yogyakarta 55584, Indonesia

*Corresponding author: Tel: +62 274 896439 ext. 3029, E-mail: isfatimah@uii.ac.id

Received: 1 February 2016;

Accepted: 31 May 2016;

Published online: 10 August 2016;

AJC-17998

This study aimed to investigate the physico-chemical properties of Pt dispersed in Al and Zr pillared saponite and montmorillonite. The chemical and morphological characteristics of prepared materials were carried out by using X-ray diffraction, scanning electron microscopy and Lewis to Brønsted acidity ratio (L/B) by pyridine adsorption followed by Fourier transform infrared analysis methods. The BET surface analysis results showed that the specific surface area of clays increased by Al and Zr pillarization and then reduced after Pt dispersion. Solid acidity and L/B as important features for the catalytic activity was increased significantly by modifications. The catalytic activity in citronellal conversion feasibility of the materials was examined systemically by evaluating the effects of pillarization and Pt dispersion on bifunctional catalytic activity of citronellal conversion by a tandem cyclization-hydrogenation conversion assisted by microwave irradiation. Bifunctionality of the catalysts in the catalytic testing was indicated from the total conversion parameter as well as selectivity to produce isopulegol and menthol from cyclization and cyclization-hydrogenation schemes. It is suggested that the presence of Pt in catalyst plays important role for hydrogenation step in producing menthol.

Keywords: Cyclization, Hydrogenation, Pillared clay, Pillarization, Platinum.

INTRODUCTION

Clays are known as one of the inorganic materials with some applications especially as catalyst and adsorbent in industries. The potency of porosity and also modifiable structure of clays have been reported as high potential for developing smart inorganic materials. For those purposes, clays particularly smectite class are modified related to their application [1-3]. Smectite clays are modified with metals or oxides in order to enhance the activity regarding to the specific catalytic reactions instead of to cover the limitation related to its lack of the structure stability in high temperature. Metal oxide pillared clays are popular method in clay modification scheme. The pillarization process consists of the metal oxide insertion between the interlayer region of clays and have been reported to give sufficiently thermal stability. Among some metal oxide such as Ti, Cr, Zr and Zn, Al and Zr were intensively reported for catalysis purposes [4-8]. Preparation of Al- and Zr-pillared smectite involving pillared montmorillonite and pillared saponite were reported to be active as catalyst in many reactions such as hydrogenation, esterification, *etc.* Not only as catalysts itself, both materials are potential to be utilized as catalyst support from their thermal stability and easily prepared. In previous works Al-pillared montmorillonite (Al-PILM) was reported to have high catalytic activity in hydro-

cracking reaction and in other scheme it were reported to be good support for Ti, Ce, Pt and Fe catalysts, while Zr-pillared montmorillonite (Zr-PILM) was reported actively support Ni and Fe catalysts for some catalytic applications significantly [3,9-13].

The use of heterogeneous catalysts with the combination of microwave irradiation to make a green scheme of chemistry catalysis are widely developed. Among so many microwave assisted organic reactions, a microwave assisted tandem cyclization-hydrogenation reaction of citronellal directly to menthol is an important pathway in chemical industry since menthol demand is very high [14-16]. A bifunctional catalyst play important role within the mechanism and technique. A catalyst with dual properties; acidity and capability to conduct hydrogenation are a must properties. By considering the hydrogenation activity of Pt and in other side it is very expensive to be applied with a pure form. The dispersion of Pt in a stable inorganic support of clays and pillared clays are attempted in this research. Study focused on the physico-chemical character of platinum dispersed materials and its effect on catalytic activity.

EXPERIMENTAL

Materials used in this research consist of saponite (Sp) from Kunimine Industry, Japan that was used as received, natural montmorillonite (Mt) from Pacitan, East Java,

Indonesia that was acid activated by refluxing in sulfuric acid 1 M for 6 h before filtration and neutralization. Aluminium chloride hexahydrate, hexachloro platinum acid, sodium hydroxide, zirconium chloride hexahydrate were purchased from Merck-Millipore while citronellal, isopulegol and menthol were obtained from Sigma-Aldrich.

Zirconium and aluminium pillarization onto saponite and montmorillonite pillared were conducted by a known synthetic procedure using zirconium oxide chloride and aluminium-chloride hexahydrate as source of Zr and Al, respectively [5-7]. Briefly, the aluminium-pillared clay (Al-PILC) was prepared by intercalating with an oligomeric solution previously made from slow titration of NaOH to aluminium chloride solution with a $^{-}\text{OH}/\text{Al}$ ratio of 2:2 followed by centrifugation. In the case of zirconium-pillared clay (Zr-PILC), the oligomeric intercalation solution was prepared from a 0.1 M ZrOCl_2 solution. The dispersion of both Al and Zr precursor were performed by dropping the precursor into clay suspension in water (5 wt. %) under stirring. The molar to mass ratio of Al/clay and Zr/clay was setting up at 40 mmol/g followed by further stirring, washing, neutralization and drying at 100 °C for a night in order to remove water from the solid. Calcination of dry solid was then conducted at 400 °C under a flow of dry air. The solids obtained by these steps are called as Al-PILS, Zr-PILS, Al-PILM and Zr-PILM, respectively with PILS and PILM are designated for pillared saponite and montmorillonite terminology.

The PILMs and PILSs supported platinum catalysts were prepared by the impregnation method. A suitable amount of the aqueous solution of H_2PtCl_6 was added into the support material. After stirring for 24 h, the solids obtained were dried and calcined by a temperature programmed from room temperature to 400 °C at a heating rate of 2 °C/min and kept for 4 h, then followed by flowing H_2 gas at 200 °C for 5 h. The theoretical content of Pt in each of the catalyst is varied at 0.25 and 0.50 % wt. The catalysts are labeled as using Pt-0.1 and Pt-0.4 codes followed by the supports codes.

Preparation of Pt-montmorillonite and saponite were also engaged in order to have reference material for catalytic activity test. For this H_2PtCl_6 solution was utilized as precursor and the Pt content was set up at 0.10 and 0.40 % wt. of clays. The solution was dispersed slowly into clay suspension followed by stirring for 24 h. In order to compare the effect of Pt and raw clays, the preparation of Pt dispersion onto both clays was also conducted by using impregnation process (prepared material furthermore called as Pt/Mt and Pt/Sp). The solution of H_2PtCl_6 in water was slowly added into the suspension of clays in water (5 % wt.) under the stirring and was continued until 24 h. The obtained mixture was dried by heating at 100 °C without filtration, washing and neutralization steps. Dried solid was grinded and then calcined at 400 °C.

Characterization of materials was studied by some measurements consist of X-ray diffraction (XRD) analysis by mean Shimadzu X6000 instrument. The surface areas, pore volumes and pore radius data were determined from nitrogen adsorption isotherms measured at liquid nitrogen temperature using an ASAP 2100 sorptometer (Micromeretics). The surface acidity of the catalysts was measured by quantitative total

surface acidity by back titration method using *n*-butylamine as standard and also qualitatively by pyridine adsorption followed by Fourier transform infrared analysis. Total surface acidity was calculated by measuring adsorbed/interacted *n*-butylamine with the solid after mixing an excess *n*-butylamine solution and the catalyst powder under stirring for a night. By using back titration using citric acid as standard the total acidity was counted as mmol butylamine per gram of catalyst [17,18]. Qualitatively, procedure An AVATAR FTIR spectrophotometer instrument was utilized to determine the peak of adsorbed pyridine on surface as probe molecule to detect surface acidity. The powder was firstly evacuated before purged with pyridine vapour for a night. Adsorbed pyridine was identified by FTIR measurement. Lewis to Brønsted (L/B) ratio was determined by following equation:

$$L/B = I_{1450-1455 \text{ cm}^{-1}}/I_{1540-1560 \text{ cm}^{-1}} \quad (1)$$

with $I_{1450-1455 \text{ cm}^{-1}}$ = intensity of the band at 1450-1455 cm^{-1} and $I_{1540-1560 \text{ cm}^{-1}}$ = intensity of the band at 1540-1560 cm^{-1} .

Performance of prepared catalysts was tested in citronellal conversion carried out on a microwave reactor. Catalyst samples (0.02 g) were mixed with the reactant citronellal (10 mmol) and ammonium formate (40 mmol) in isopropanol solvent. The reactions were conducted for 15 min irradiation. In order to evaluate the activity of the catalysts, total conversion and selectivity to produce isopulegol ($S_{\text{isopulegol}}$) and menthol (S_{menthol}) products was evaluated by following formula:

$$\text{Conversion (\%)} = \frac{[\text{Citronellal}]_0 - [\text{Citronellal}]_{\text{product}}}{[\text{Citronellal}]_0} \times 100 \quad (2)$$

$$S_i (\%) = \frac{[\text{Selected product}]}{[\text{Total product}]} \times 100 \quad (3)$$

RESULTS AND DISCUSSION

Hypothetical structure of the materials represent the homogeneous distributed Pt into pillared clays (Zr-PILM, Zr-PILS, Al-PILM and Al-PILS). Effect of Pt dispersion to the structure of materials was studied by XRD analysis, gas sorption analysis, solid acidity and also surface morphology by SEM profile.

Fig. 1 exhibits XRD reflections of the materials. It is observed that there are some reflections indicate the presence of montmorillonite at $2\theta = 5-6, 5^\circ$ (d_{001}), $2\theta = 19, 89^\circ$ (d_{002}) and $2\theta = 35, 5^\circ$ (d_{006}). Details of the change of d_{001} values along the modifications is listed in Table-1.

The basal spacing d_{001} of montmorillonite (14.58 Å) and saponite (12.44 Å) increases as pillarization using either by Al or Zr, but both for montmorillonite and saponite, Pt dispersion give no significant change of d_{001} . Zirconium pillarization of montmorillonite and saponite exhibits the formation of tetragonal ZrO_2 phase as shown by the reflections at $2\theta = 30^\circ$ and 50° while from Al pillarization there is no new reflection correlated with the presence of new phase. Conversely with Al and Zr pillarization Pt dispersion also affect to decrease the intensity of d_{001} reflection indicating decreasing crystallinity. Similar effect is also gained by Pt dispersion onto Al and Zr pillared clays.

TABLE-1
 d_{001} AND FWHM OF [001] REFLECTION OF THE MATERIALS

Sample	d_{001} (Å)	FWHM (nm)	Sample	d_{001} (nm)	FWHM (nm)
Mt	14.58	0.05	Sp	12.44	0.79
Al-PILM	15.67	0.39	Al-PILS	14.63	0.51
Zr-PILM	16.50	0.44	Zr-PILS	14.60	0.54
Pt-0.4/Mt	13.78	0.78	Pt-0.4/Sp	13.52	0.34
Pt-0.1/Mt	14.47	0.42	Pt-0.1/Sp	13.67	0.67
Pt-0.1/Al-PILM	15.67	0.66	Pt-0.1/Al-PILS	12.45	0.87
Pt-0.4/Al-PILM	15.45	0.64	Pt-0.4/Al-PILS	11.98	0.77
Pt-0.1/Zr-PILM	16.45	nd	Pt-0.1/Zr-PILS	nd	nd
Pt-0.4/Zr-PILM	15.85	nd	Pt-0.4/Zr-PILS	nd	nd

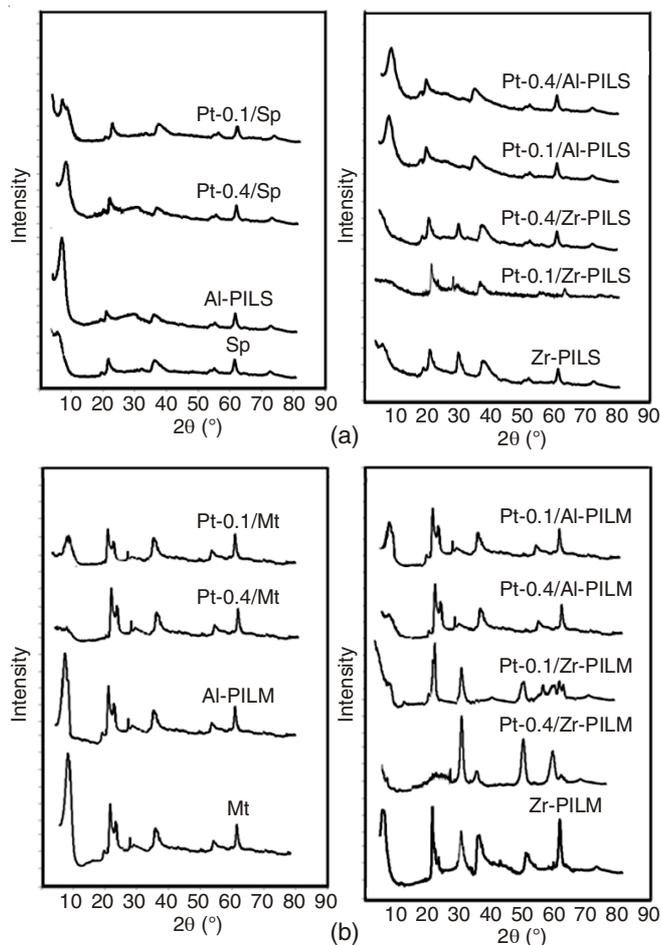


Fig. 1. XRD pattern of (a) Pt dispersed pillared saponites and raw saponite (b) Pt-dispersed pillared montmorillonite and raw montmorillonite

The acidity of H_2PtCl_6 may cause the clays structure delamination of clays and pillared clays. By two variation of Pt concentrations, it is found that the Pt content give no significant different effect to the structure of catalysts. The compared content of important component in materials listed in Table-2 also indicated that Zr and Pt immobilized by pillarization and dispersion onto montmorillonite and saponite give similar additional amount.

Increasing specific surface area of materials was gained by pillarization using three metals precursors but then after Pt dispersion onto pillared clays the surface area are getting reduced (Table-3). It may cause by the destruction of the structure as shown by XRD measurement so the formation of porous structure is gained by pillarization was collapsed. In

general the surface area of pillared saponite is more retained compared to that of pillared montmorillonites. The change on structure was also affect to the surface profile of the materials such as depicted from compared surface profile in Fig. 2. A layer surface profile is exposed by raw saponite and before was pillared with Zr and Pt it became rougher. The change of surface profile is also indicated from the adsorption-desorption pattern shown by the pattern presented in Fig. 3.

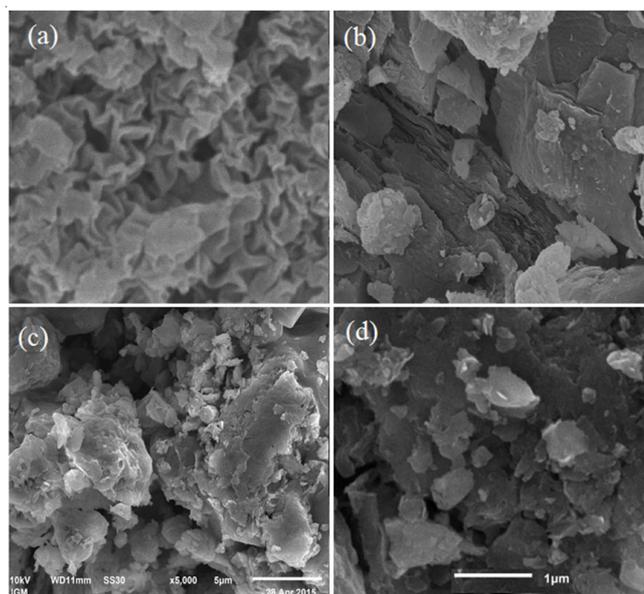


Fig. 2. SEM profile of (a) SAP (b) Al-PILS (c) Pt-0.4-PILS (d) Pt-0.4/Zr-PILS

There is an evolution of the adsorption-desorption pattern related to the composition of microporous and mesoporous structure in the materials. The attachment of Pt and Zr affect to increase the Lewis acidity *via* the availability of adsorption sites from *d*-orbital of Pt and Zr on surface as also reported in many previous investigation. The higher elevation of both total acidity and L/B ratio of the catalyst is also confirmed the higher potency of Zr and Pt to enhance the acidity compared to Al. Fig. 4 depicts the compared FTIR spectra of some samples after pyridine adsorption. The broad bands observed at around $3455-3400\text{ cm}^{-1}$ signify the $-OH$ stretching vibrations of the $H-O-H$, $Si-OH$ and $Al-OH$ groups from the silica-alumina structure of montmorillonite. The existence of silica is also indicated by finger print bands at around $500-450\text{ cm}^{-1}$. The spectral bands at 1640 cm^{-1} also represent to the $\delta(H-O-H)$ of water. The presence of adsorbed pyridine was recorded

TABLE-2
ELEMENTAL ANALYSIS RESULTS OF MATERIALS

Sample	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	Zr	Pt	CEC (meq/100 g)
Mt	8.33	2.82	21.9	59.8	nd	nd	68.90
Al-PILM	2.31	1.09	34.5	41.1	nd	nd	45.80
Zr-PILM	1.11	1.00	19.67	47.78	11.34	nd	48.98
Pt-0.1/Mt	0.91	1.03	18.66	36.98	nd	0.39	35.42
Pt-0.4/Mt	0.89	0.89	19.56	33.56	nd	0.11	36.09
Pt-0.1/Al-PILM	0.99	0.87	29.78	42.12	nd	0.10	30.23
Pt-0.4/Al-PILM	0.34	0.98	28.87	43.09	nd	0.38	30.02
Pt-0.1/Zr-PILM	0.23	1.03	21.06	27.98	10.20	0.12	29.90
Pt-0.4/Zr-PILM	0.23	0.88	20.98	28.09	10.82	0.11	29.87
Sp	3.75	30.88	6.99	58.57	nd	nd	99.84
Al-PILS	2.09	22.09	20.89	48.78	nd	nd	67.09
Zr-PILS	2.26	28.76	7.09	35.67	10.98	nd	64.30
Pt-0.1/Sp	2.05	28.11	6.99	59.78	nd	0.44	78.09
Pt-0.4/Sp	1.79	29.09	6.99	56.92	nd	0.12	88.34
Pt-0.1/Al-PILS	1.59	22.39	19.67	49.03	nd	0.10	61.10
Pt-0.4/Al-PILS	1.09	21.11	20.48	48.98	nd	0.39	59.08
Pt-0.1/Zr-PILS	1.96	27.86	8.09	32.89	10.42	nd	55.11
Pt-0.4/Zr-PILS	2.01	29.02	9.01	33.67	10.68	nd	54.06

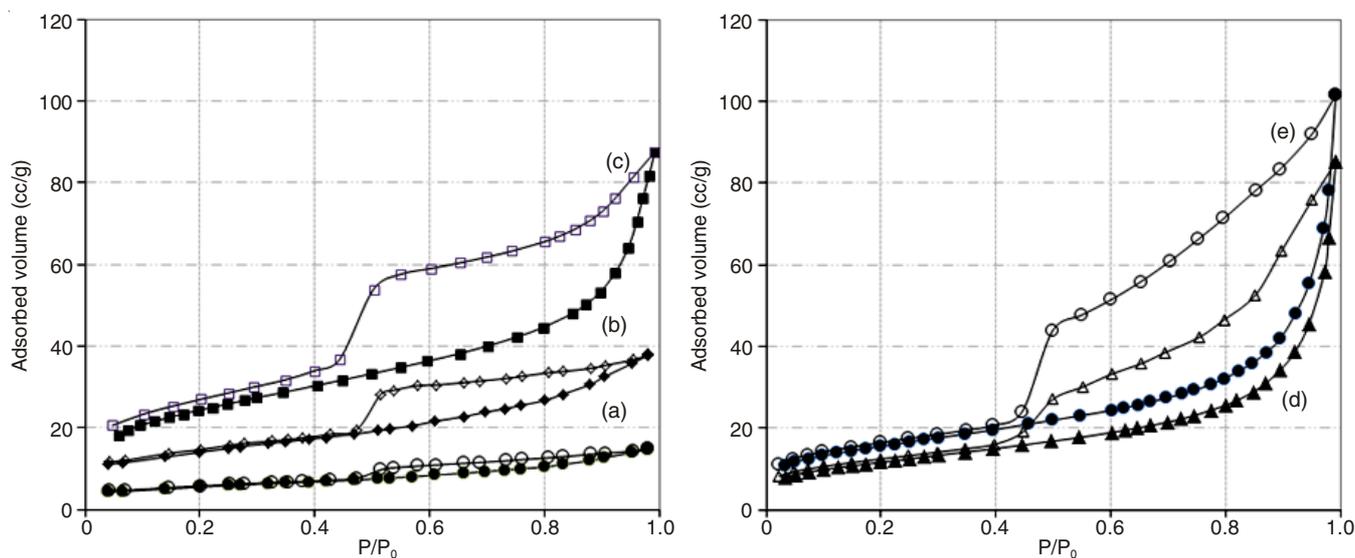


Fig. 3. Adsorption-desorption pattern of (a) Mt (b) Al-PILM (c) Zr-PILM (d) Pt-0.4/Mt and (e) Pt-0.4/Mt

TABLE-3
SURFACE PROFILE PARAMETERS, SOLID ACIDITY AND L/B OF MATERIALS

Sample	Pore radius (Å)	Specific surface area (m ² /g)	Pore volume (10 ⁻³ cc/g)	Total acidity	L/B
MMT	7.98	45.42	0.521	0.775	0.855
Al-PILM	8.20	97.50	16.94	1.323	1.035
Zr-PILM	8.90	149.87	43.32	1.455	1.047
Pt-0.1-PILM	7.90	101.09	20.09	1.480	1.099
Pt-0.4-PILM	8.03	99.09	19.98	1.497	1.010
Pt-0.1/Al-PILM	8.13	66.65	21.12	1.234	1.030
Pt-0.4/Al-PILM	8.12	60.21	20.13	1.563	1.045
Pt-0.1/Zr-PILM	5.79	54.23	21.57	1.345	1.043
Pt-0.4/Zr-PILM	6.24	49.62	21.55	1.344	1.044
Saponite	11.02	199.45	28.97	1.053	1.108
Al-PILS	10.90	261.49	42.73	1.304	1.112
Zr-PILS	12.30	234.54	32.56	1.432	1.208
Pt-0.1-PILS	11.09	200.098	29.05	1.455	1.108
Pt-0.4-PILS	11.45	208.45	33.02	1.451	1.107
Pt-0.1/Al-PILS	10.54	79.87	24.45	1.523	1.126
Pt-0.4/Al-PILS	10.47	66.23	24.03	1.539	1.121
Pt-0.1/Zr-PILS	9.06	99.54	28.97	1.623	1.205
Pt-0.4/Zr-PILS	9.89	89.89	28.34	1.664	1.209

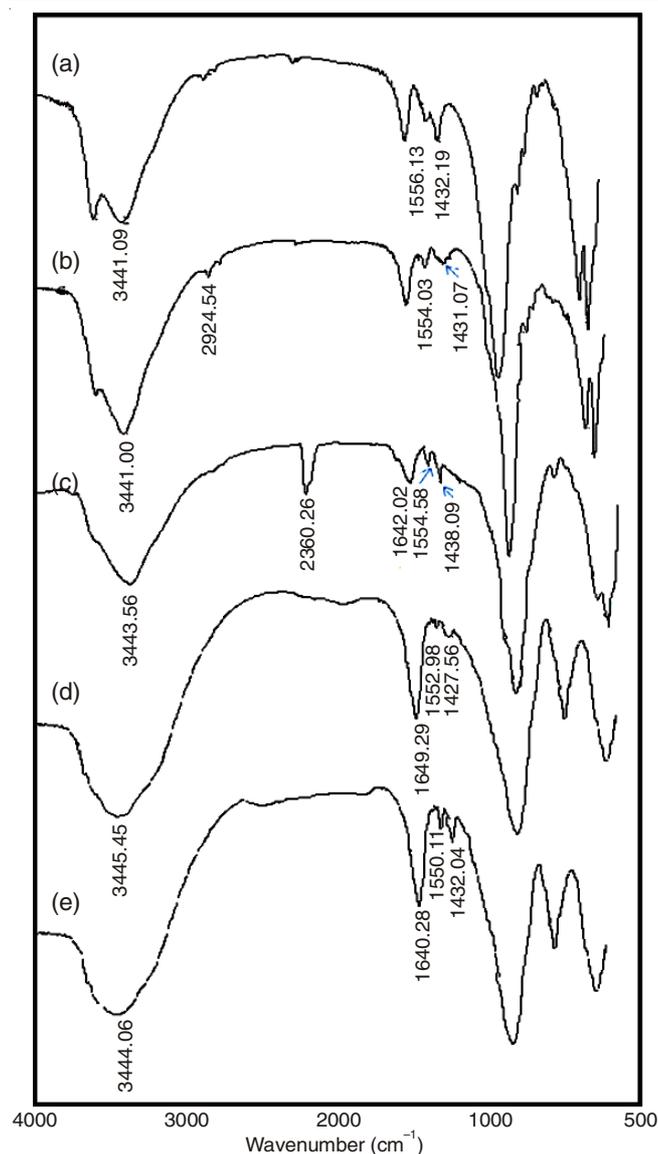


Fig. 4. FTIR of samples after pyridine adsorption (a) Mt (b) Al-PILM (c) Zr-PILM (d) Pt-0.4/Mt and (e) Pt-0.4/Zr-PILM

by peaks at around 1540 cm^{-1} and 1450 cm^{-1} . From the spectra of modified montmorillonite it is observed that compared to montmorillonite, the attachment of Zr and Pt give the shifting of the spectra at around 3400 cm^{-1} into the higher wavenumber as representation of the higher vibration energy of possible Si-OH and Al-OH from the interaction with Zr and Pt.

The basic idea of L/B measurement is arise from the possible interaction between pyridine species as expressed in Fig. 5. Species I (Lpy) can be formed by coordination bond of pyridine's electron pair with the empty orbitals of metals on materials surface. Species II (Br-py) is pyridinium ion formed from the transfer of H^+ form Brønsted acidity $-\text{OH}^{2+}$ of solids with pyridine and species III (Hpy) is formed from hydrogen bond from N and $-\text{OH}$ from clay's structure. The vibration indicating the presence of pyridine appeared at around $1700\text{--}1400\text{ cm}^{-1}$. The band at 1640 cm^{-1} is assigned to the presence of BpPy and at the other at around $1455\text{--}1450\text{ cm}^{-1}$ is characteristic towards Lpy [19].

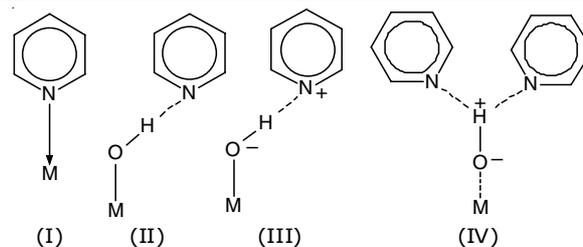


Fig. 5. Model of acid-base interaction between pyridine and surface

Catalytic activity data of materials (Table-4) suggest the improving catalytic activity correspond to pillarization and afterward Pt dispersion onto pillared clays. Basically the mechanism of citronellal conversion into menthol is preferred. Isomerization occurs at the first step to convert citronellal to isopulegol followed by hydrogenation of isopulegol into menthol. In this catalytic activity set up both isomerization and hydrogenation are designed to be conducted in a one pot system in a microwave assisted reaction. Ammonium formate was utilized as catalytic hydrogen transfer agent. The higher conversion as well as the higher selectivity of menthol product will indicate the bifunctionality of the catalysis mechanism as stated in Fig. 6.

TABLE-4
CATALYTIC ACTIVITY DATA OF CATALYSTS

Sample	Conversion	$S_{\text{isopulegol}}$	S_{menthol}
Mt	66.45	3.45	0
Al-PILM	88.45	4.55	0
Zr-PILM	90.34	5.98	0
Pt-0.1/Mt	99.98	26.57	3.334
Pt-0.4/Mt	99.99	28.88	4.090
Pt-0.1/Al-PILM	93.99	10.98	4.230
Pt-0.4/Al-PILM	94.99	10.97	4.340
Pt-0.1/Zr-PILM	95.51	11.52	4.670
Pt-0.4/Zr-PILM	96.76	12.78	4.980
Sp	68.03	4.56	0
Al-PILS	89.08	5.90	0
Zr-PILS	90.34	13.67	3.210
Pt-0.1/Sp	99.56	13.95	4.050
Pt-0.4/Sp	99.99	14.08	5.670
Pt-0.1/Al-PILS	95.98	14.45	9.870
Pt-0.4/Al-PILS	97.78	14.86	9.990
Pt-0.1/Zr-PILS	99.56	14.99	10.56
Pt-0.4/Zr-PILS	99.45	15.03	11.08

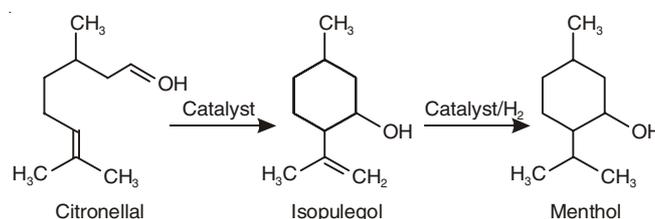


Fig. 6. Catalytic steps of citronellal conversion

Total conversion is associate with both isomerization and hydrogenation steps while the selectivity toward menthol product indicate the function of hydrogenation step that is correlated with the activity of Zr and/or Pt of catalyst.

Important conclusion from the data (Table-4) is that in general modified clays give higher total conversion of

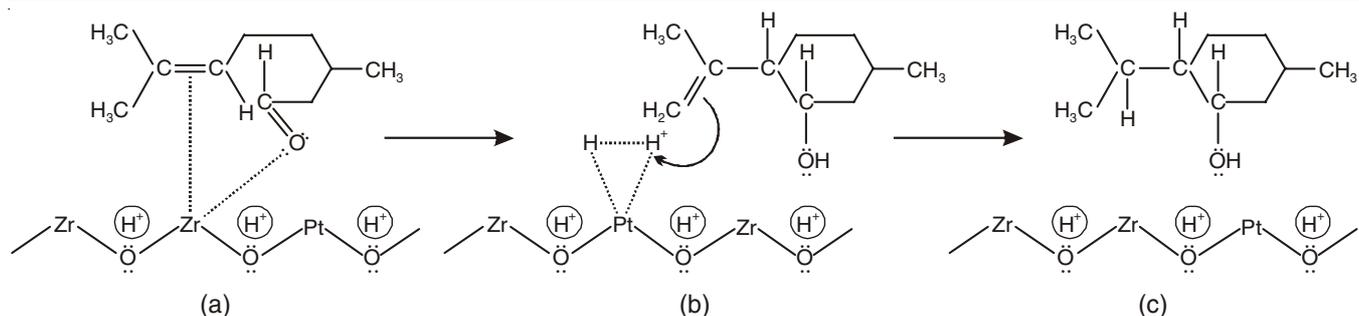


Fig. 7. Schematic representation of citronellal conversion (a) cyclization step over Zr as active site (b) hydrogenation step with Pt active site (c) product desorption

citronellal confirming the effect of improving solid acidity to increase the conversion. The comparison between aluminium-pillared clays, zirconium-pillared clays and also platinum-pillared clays show that the higher solid acidity the higher total conversion. Furthermore it is seen that bifunctional function of Zr and Pt in citronellal conversion as shown by the formation of menthol in the product while catalysts without both metal give no menthol product. It is noted that effect of specific surface area, pore volume and pore radius is not clearly linear with the total conversion and also selectivity to produce isopulegol and menthol. The condition of the reaction system which mainly influenced by the acidity and the presence of bifunctional system may be the main reason for this data. However by comparing the content of Pt in the catalysts the higher Pt content contributes to the increasing selectivity to menthol product. By comparing Pt/clays and Pt dispersed onto pillared clay, it is confirmed that Pt dispersed onto Zr-pillared clays exhibit the higher activity as indicated by the higher total conversion as well as selectivity to produce menthol. The data suggests that the activity of Zr in isomerization as first step before menthol conversion. Schematic representation of zirconium catalysis for isopulegol is presented in Fig. 7.

Conclusions

In this study, smectite consist of montmorillonite and saponite modification by using Al and Zr pillarization followed by Pt dispersion was confirmed by XRD measurement, BET surface analysis, SEM technique and solid acidity evaluation. Catalytic activity of prepared materials was studied on citronellal conversion by using microwave assisted reaction. The obtained results can be summarized as follows:

- By the pillarization the specific surface area of smectite was increased considerably but after Pt dispersion the surface area tends to be reduced.
- Increasing solid acidity is gained by both pillarization and Pt dispersion.
- The presence of Pt in catalysts play role as bifunctional catalyst refer to hydrogenation active capability in producing menthol in a tandem cyclization-hydrogenation system.

ACKNOWLEDGEMENTS

The authors thank The World Academy of Sciences (TWAS) for research grant 14-036 RG/CHE/AS_I-UNESCO 324028570.

REFERENCES

1. N.R. Sanabria, R. Molina and S. Moreno, *Int. J. Photoenergy*, **Article ID 864104** (2012).
2. A. Aznárez, R. Delaigle, P. Eloy, E.M. Gaigneaux, S.A. Korili and A. Gil, *Catal. Today*, **246**, 15 (2015).
3. E.A. Emam, *ARNP J. Sci. Technol.*, **3**, 356 (2013).
4. H. Lu, X. Yang, G. Gao, K. Wang, Q. Shi, J. Wang, C. Han, J. Liu, M. Tong, X. Liang and C. Li, *Int. J. Hydrogen Energy*, **39**, 18894 (2014).
5. M.L. Pinto, J. Marques and J. Pires, *Sep. Purif. Technol.*, **98**, 337 (2012).
6. M.L. Pinto and J. Pires, *Micropor. Mesopor. Mater.*, **151**, 403 (2012).
7. A.H. Pizarro, V.M. Monsalvo, C.B. Molina, A.F. Mohedano and J.J. Rodríguez, *Chem. Eng. J.*, **273**, 363 (2015).
8. N. Tangchupong, W. Khaodee, B. Jongsomjit, N. Laosiripojana, P. Praserttham and S. Assabumrungrat, *Fuel Process. Technol.*, **91**, 121 (2010).
9. G.H. Wang, M.D. Sun, W.B. Li, Y.Z. Lu, X.Q. Liu, J. Wang, H. Hu, Q. Liu and T.T. Huang, *Adv. Mater. Res.*, **581-582**, 723 (2012).
10. J. Li, Z. Jiang, Z. Hao, X. Xu and Y. Zhuang, *J. Mol. Catal. Chem.*, **225**, 173 (2005).
11. A. Gil, M.A. Vicente, J.-F. Lambert and L.M. Gandía, *Catal. Today*, **68**, 41 (2001).
12. N.R. Sanabria, M.A. Centeno, R. Molina and S. Moreno, *Appl. Catal. A*, **356**, 243 (2009).
13. V. Ramaswamy, S. Malwadkar and S. Chilukur, *Appl. Catal. B*, **84**, 21 (2008).
14. P. Mertens, F. Verpoort, A. Parvulescu and D. Devos, *J. Catal.*, **243**, 7 (2006).
15. K.A. da Silva Rocha, P.A. Robles-Dutenhefner, E.M.B. Sousa, E.F. Kozhevnikova, I.V. Kozhevnikov and E.V. Gusevskaya, *Appl. Catal. B*, **317**, 171 (2007).
16. A.M. Balu, J.M. Campelo, R. Luque and A.A. Romero, *Org. Biomol. Chem.*, **8**, 2845 (2010).
17. D.T. Yazici and C. Bilgiç, *Surf. Interface Anal.*, **42**, 959 (2010).
18. M. Yurdakoc, M. Akcay, Y. Tonbul and K. Yurdakoc, *Turk. J. Chem.*, **23**, 319 (1999).
19. B. Tyagi, C. Chudasama and R. Jasra, *Appl. Clay Sci.*, **31**, 16 (2006).