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Pt dispersed on sulfated-zirconium pillared saponite as catalyst in citronellal conversion

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Abstract

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. The catalytic activity can be generated by modification of the silica-alumina framework by elements having Lewis acidity such as Ti and Zr. On the other side, menthol is an important chemical compound in cosmetics and toiletries industries. A way to obtain menthol is hydrogenation of isopulegol. Isopulegol itself can be converted from citronellal. In a previous work we demonstrated the conversion of citronellal to isopulegol using Ti and Zr pillared clay using montmorillonite clay as raw material. In the present work we extend the applicability of pillared clay materials as support of bifunctional heterogeneous catalysts, to produce other intermediates and also menthol in a one pot conversion system as called as a tandem cyclization-hydrogenation. A bifunctional catalysts from Pt immobilized Zr-pillared clay derived from saponite as raw clay were prepared. Furthermore the relation between physicochemical characters and catalytic activity in citronellal conversion was studied. Reaction conversion, catalyst activity, selectivity to a certain product, reusability and kinetic study of the reaction were evaluated based on the term of green conversion principles.

Keywords: Pillared clay; Pt; Catalytic hydrogen transfer; Menthol.

1. Introduction

Menthol is one of important chemical product for pharmacy and toiletries industries. Since demand on menthol increases from time to time, the production of menthol from the extraction of origin plant *Mentha arvensis* is not enough to cover the industry demand (Chan et al., 2004). Methods for synthesize menthol from other source are widely investigated. An important route for this synthesis is the conversion from citronellal via isopulegol as intermediate. Selective hydrogenation of isopulegol is important step in citronellal conversion into menthol that is conventionally conducted in two steps: isomerization of citronellal followed by hydrogenation. In particular, the hydrogenation step needs special condition as well as selective catalyst for this process. Conventionally the process can be conducted by hydrogenation under high pressure but it is time consuming work. It is not only high energy consuming process but also an inefficient process. These are the reason why some investigations were focused on safer and greener routes and techniques (Badam, 2008; Ravasio et al., 2000). Based on numerous investigations on the use of catalytic hydrogen transfer for selective hydrogenation of unsaturated carbon bond and considering that from previous study the conversion and selectivity of isopulegol from citronellal over Pt-modified montmorillonite is high, in the present work one pot citronellal conversion and catalytic hydrogen transfer of citronellal into menthol was studied. Among some metal potential in one pot isomerization-hydrogenation reaction, Pt is popular catalyst especially as hydrogen agent (Figueiredo et al., 2011). On the other side, previous researches reported the excellent improvement of clay based catalyst by zirconium pillarization and sulfation toward zirconium-pillared clay consisting of montmorillonite and saponite (Fatimah et al., 2014; Fatimah et al., 2015). Research is aimed to study the change in physicochemical character of Pt dispersed onto sulfated zirconium-pillared clay corresponding to the catalytic activity in citronellal conversion activity. Synthetic saponite was chosen as clay mineral for catalyst preparation.

2. Materials and method

The Pt/S-Zr/saponite (hereafter indicated as Pt/S-Zr/Sap) was prepared by impregnation method. Hexachloroplatinic hexahydrate was used as precursor. A solution of hexachloroplatinic was dispersed into S-Zr/Saponite (S-Zr/Sap) suspension at the theoretic Pt ratio of 3% wt. S-Zr/Sap was prepared by saponite pillarization by mixing zirconium oxide chloride precursor solution followed by stirring, washing and calcination at 400 °C for 4 hours. Precursor solution was prepared by diluting zirconium oxide chloride with the addition of Ba in the Zr/Ba mole ratio of 5:1 in water. The mixture was stirred for 4 h. The solution was then slowly dispersed into saponite at the Zr/saponite mole /weight ratio of 5 mmol/100 g followed by refluxing for 6 h. The mixture was then filtered, dried and calcined under N₂ flow at 400 °C for 5h. Sulfation was conducted by solid reaction of Zr/saponite with ammonium sulfate refer to previous works in the synthesis of sulfated-zirconia pillared montmorillonite and sulfated zirconia. The mixture was than calcined at 400 °C for 4 h. The solid obtained from these step was then added with NaBH₄ as reducing agent followed by stirring for 5 h and re-drying and grinding to get the powder of Pt/S-Zr/Sap. All prepared and raw materials were characterized by X-ray diffraction (XRD), gas sorption analysis and surface acidity. Total solid acidity was determined by n-butylamine back titration method while Brønsted to Lewis acidity ratio was measured by using pyridine

adsorption followed by Fourier-Transform Infra Red (FTIR) spectrometry using a procedure reported in a previous work (Fatimah et al., 2014).

For the catalytic activity test two methods, conventional method (Conv.) and microwave assisted catalytic hydrogen transfer method (MW), were employed. In Conv. method the reaction was performed in a batch reactor. Mixture of citronellal and catalyst in the reactor was flushed with 2 kPa hydrogen for 10 h at temperature of 150 °C. MW method condition was the same used in the Conv. Citronellal was added with ammonium formate as hydrogen transfer agent followed by microwave irradiation for 15 min. Results was analyzed by gas chromatography-mass spectra (GCMS) to evaluate total conversion and selectivity to produce menthol by the following equations:

$$\text{total conversion} = \frac{[\text{citronella}]_{\text{initial}} - [\text{citronella}]_{\text{product}}}{[\text{citronella}]_{\text{initial}}} \times 100\%$$

$$\text{selectivity to menthol} = \frac{[\text{menthol}]}{[\text{products of reaction}]} \times 100\%$$

The concentration of citronellal, menthol and other product were calculated based on chromatogram peaks.

3. Results and discussion

Nitrogen sorption isotherm of prepared materials compared to raw materials (Fig. 1) shows representative type IV curves with H3 hysteresis loops, meaning the sample has typical slit-type mesopores generated by the interparticle porosity of layers morphology. A step step occurs at approximately $P/P_0 = 0.80 - 0.98$ owing to capillary condensation. The pore-size distribution curve (Fig. 1) reflects the change in porosity respect to the pillarization and Pt impregnation and those affects the specific surface area, pore volume and pore radius tabulated in Table 1.

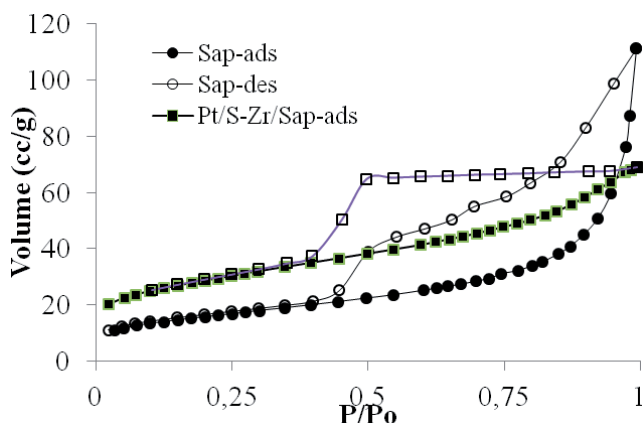


Fig. 1. Nitrogen adsorption-desorption profile of materials.

Table 1. Specific surface area, pore volume and pore radius of the prepared material.

Sample	Specific surface area (m ² /g)	Pore Volume (cc/g)	Pore Radius (Å)
SAP	170.96	38.924	14.58
Pt/S-Zr/SAP	87.89	19.22	11.09

The surface area of saponite is 267.96 m²/g. After pillarization with ZrO₂ the specific surface area increased to 323.81 m²/g. Surface blocking with Pt particles was indicated by decreasing specific surface area and pore volume parameter. Pt/S-Zr/Sap exhibits lower volume compared to SAP at all pore radius range, while in SAP sample micropores are dominantly contained.

The change in specific surface area is in line with XRD data presented in Fig. 2.

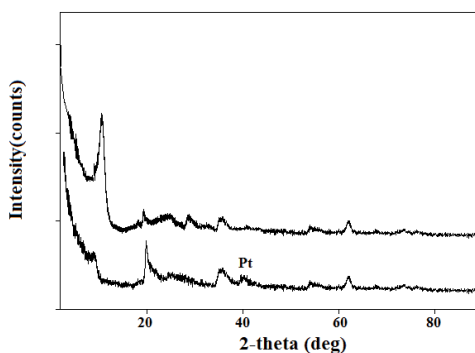


Fig. 2. XRD pattern of materials.

Presence of dispersed Pt is documented by the reflection corresponding to Pt(111) at $2\theta = 40^\circ$ (Jiang et al., 2011). This data is confirmed by SEM-EDX analysis. The change of d_{001} spacing during the preparation is reported in Table 2.

Table 2. d_{001} value of XRD measurement.

Sample	2θ (°)	d_{001} (Å)
SAP	5.22	17.97
Pt/S-Zr/SAP	5.14	18.25

Pt-saponite correspondingly appears to have rougher surface and Pt particles can be detected from the specified grain objects on surface. EDS spectra reveals the Pt content of 5.02% wt., slightly higher than theoretic content in the synthesis (5% wt.). Clay weight loss during thermal treatment was considered as the cause of the rest Pt content in prepared material. Effect of Pt insertion to the surface acidity can be seen by total acidity measurements. The measurements consist of total acidity determination by using n-butylamine back titration method and for Brønsted to Lewis acidity ratio (B/L) pyridine adsorption followed by FTIR spectroscopy measurement was examined. The results are presented in Table 3 and Fig. 3.

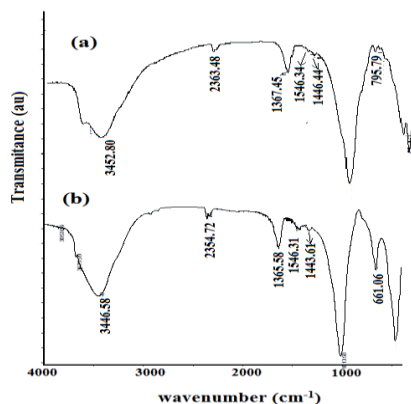


Fig. 3. FTIR of pyridine-adsorbed materials.

It can be seen (Table 3) that the presence of Pt in Pt-saponite demonstrate the higher total acidity and lower B/L ratio suggesting that Pt contributes to enhance the Lewis acidity. This is theoretically and directly correlate with the catalytic activity in such isomerization reaction. Furthermore, Pt is selective to hydrogenation reactions.

Table 3. Solid acidity data of prepared material.

Sample	B/L	Total Acidity
SAP	1.22	0.917
Pt/S-Zr/SAP	1.14	1.125

Catalytic activity of Pt-saponite compared to raw saponite is documented by the catalytic activity data consist of total conversion and also selectivity to produce certain products listed in Table 4. In general Pt/S-Zr/Sap contributes to enhance the total conversion by both conventional method and microwave assisted reaction.

Table 4. Data of catalytic activity test.

Catalyst	Reaction condition	Total Conversion(%)	Selectivity to produce(%)		
			isopulegol	menthol	isomenthone
Sap	Conv.10h	94.55	89.09	2.11	2.56
Sap	MW. 15 min	88.09	78.90	nd	2.34
Pt/S-Zr/Sap	Conv.10h	99.88	n.d	11.67	3.45
Pt/S-Zr/Sap	MW. 15 min	96.18	n.d	12.24	nd.

Condition: catalyst 2%wt.

The presence of Pt as active sites for hydrogenation within the conversion is clearly indicated by the data. Furthermore by comparing the reaction method it was summarized that higher conversion is achieved in conventional method. Even the data suggests that the conventional method gives higher total conversion than microwave assisted reaction, the microwave assisted reaction gives shorter time in insignificant value of both total conversion and selectivity to produce menthol.

Effect of catalyst weight to the conversion and selectivity to menthol is evidenced by curve in Fig. 4. The optimum catalyst weight is 2% wt. The lower catalyst weight affect to the limited surface interactions which linearly correspond to higher reaction rate while at

the ration more than 2% wt. both reactant and products were probably adsorbed strongly and make difficulties to give higher reaction rate in a batch system.

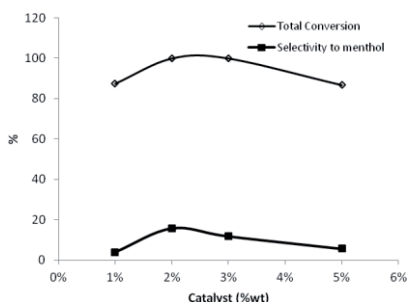


Fig. 4. Effect of catalyst weight to catalytic activity parameters.

4. Conclusion

The use of Pt/S-Zr/saponite in one-step conversion of citronellal to menthol has been realised with a yield of more than 99% and the selectivity to menthol of about 15%. The higher activity is related to increasing Lewis acidity and also to total acidity of the surface as well as to the change of catalyst physicochemical characters.

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