



Isomerization Reaction of α -Pinene Using Zirconia/Natural Zeolite Catalysts

N. WIJAYATI*, T. HANDAYANI and SUPARTONO

Department of Chemistry, Universitas Negeri Semarang, Sekaran, Gunungpati, Semarang, Indonesia

*Corresponding author: Fax: +62 24 8508035; Tel: +62 81575579586; E-mail: nanikanang@gmail.com; nanikanang@mail.unnes.ac.id

Received: 30 January 2017;

Accepted: 12 April 2017;

Published online: 12 June 2017;

AJC-18426

The isomerization reaction of α -pinene from turpentine oil using heterogeneous catalysts (Zr^{4+} /natural zeolite) produces monocyclic and bicyclic compounds and other products. The purpose of this study is to investigate the effects of time, concentration of Zr^{4+} and temperature on the activity and selectivity of the catalyst. Catalyzed reactions in heterogeneous phases were performed. In heterogeneous reaction, catalyst Zr^{4+} /natural zeolite at several temperatures were used. Results indicate that the modification of the catalyst by cation Zr^{4+} increases the acidity from 2.76 to 6.64 mmol/g. It can be observed that conversions and selectivities have been explained in terms of surface acidity, structural and textural features of the modified natural zeolite determined by using X-ray diffraction and N_2 adsorption at 77 K. FT-IR spectra of adsorbed pyridine on catalysts Zr^{4+} /natural zeolite show the presence of Lewis and Brønsted acid sites.

Keywords: Natural zeolite, Isomerization, α -Pinene.

INTRODUCTION

Turpentine oil is a product widely used in the cosmetic industry as pharmaceutical raw materials, perfumes, solvents, resins and polymers [1]. Turpentine oil contains about 57-86 % α -pinene, 8-12 % 3-carene and other groups of monoterpene. The structure of α -pinene having a skeleton of bicyclo[3.3.1]heptene, in the presence of acids, easily participates in cycle opening reactions to derivatives of *p*-menthane and molecular rearrangement reactions to derivatives of bornane or fenchane [2-4]. Complex mixture are obtained resulting from isomerization.

The isomerization reaction is developed in presence of strong acid catalysts. Homogeneous catalysts have been used by most of the industry and have a negative impact in the form of hazardous acid waste, also has short comings because it is difficult to separate from product. Heterogeneous catalysts can be used as an alternative with positive opportunities related to increased yields and selectivity of the process through the α -pinene isomerization reaction. Clay, zeolites and different oxide have been used for the catalysts of isomerization of α -pinene [5-7].

Isomerization of α -pinene can produce bicyclic compound, monocyclic or other products. Severino *et al.* [8] conducted α -pinene isomerization reaction using zeolite as a catalyst and they state that Lewis acid sites on the catalyst (weaker than Brønsted sites) are beneficial for the formation of bicyclic compounds, while Brønsted sites are responsible for the

formation of monocyclic compounds. Yadav *et al.* [7] studied the reaction catalyzed by a montmorillonite pre-treated with sulfuric acid, the results obtained α -pinene conversions of 96 % with selectivity for camphene ranging 39-49 %.

Grzona *et al.* [9] using sulfated Zirconia as a catalyst preformance α -pinene isomerization reaction to produce α -pinene conversion of 17-90 %. In the present work, Zr^{4+} /ZA catalyst was selected to study the isomerization of α -pinene. The method used in dropped Zr against natural zeolite is a method of impregnation.

EXPERIMENTAL

GC Hewlett Packard 5890 Series II, GC-MS Shimadzu QP 5000, SAA Quantachrome ASiQwin 1:11, Philips XRD Expert, PANalytical XRF MiniPal 4 and FT-IR spectrophotometer Shimadzu FT-IR 8201 PC.

Natural zeolite has been activated, calcined at 400 °C for 4 h in a calcining furnace with nitrogen gas 10 mL/min. Furthermore, natural zeolite impregnated with a Zr^{4+} metal ion. Characterization of calcinated zirconia/zeolite was carried out as the same step in the activation of zeolite, which the test catalyst's acidity using ammonia and pyridine.

The isomerization of α -pinene was carried out at atmospheric pressure at 90, 120 and 150 °C in a batch reactor using three-necked 100 mL flask with magnetic stirring, a thermometer and reflux condenser. A mixture of 10 mL α -pinene and 0.5 g catalyst was added the flask. After reacting for 60, 90, 120, 150 and 180 min, the product were analyzed by the GC-MS and FT-IR.

RESULTS AND DISCUSSION

The analysis results of XRF showed that activated natural zeolite does not contain metal ions Zr^{4+} , while on the Zr^{4+}/ZA sample containing metal ions Zr^{4+} as much as 11 % (Table-1). The results of this test showed that the value of total acidity and good acidity on the surface of H/ZA higher than Zr^{4+}/ZA , that ammonia is adsorbed to the catalyst pores.

TABLE-1
DATA XRF OF H/ZA AND Zr^{4+}/ZA CATALYST

Catalysts	Concentration of Zr (%)
H/ZA	—
Zr^{4+}/ZA (10 %)	11.0
Zr^{4+}/ZA (15 %)	6.8
Zr^{4+}/ZA (20 %)	4.6
Zr^{4+}/ZA (10 %) regeneration	7.1

Diffraction pattern of H/ZA and Zr^{4+}/ZA showed that the absence changes the structure in a significant after impregnation metals. Peaks in the diffraction pattern Zr^{4+}/ZA still shaped tapered indicating that the material is crystalline and there has been a H^+ ion exchange process with Zr^{4+} so that these catalysts are stable crystalline (Fig. 1).

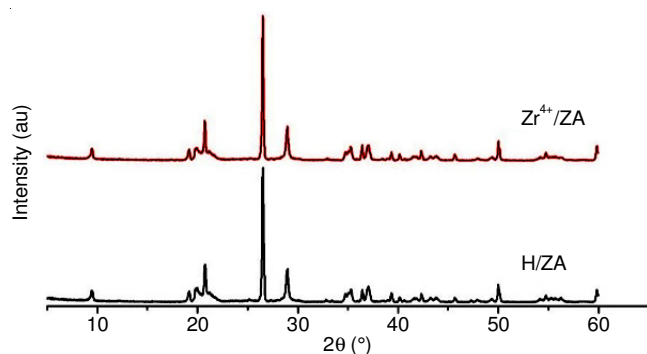


Fig. 1. Diffraction pattern of H/ZA and Zr^{4+}/ZA catalysts

X-ray diffraction pattern of the H/ZA seen a sharp peak at $2\theta = 20.76$ ($d = 4.27 \text{ \AA}$), 28.97 ($d = 3.07 \text{ \AA}$) and 50.03 ($d = 1.82 \text{ \AA}$). While based on the X-ray diffraction pattern Zr metal known to have been successfully distributed in the natural zeolite, which is characterized by peaks at $2\theta = 35.07$ ($d = 2.55 \text{ \AA}$), 50.03 ($d = 1.82 \text{ \AA}$) and 50.18 ($d = 1.81 \text{ \AA}$).

Table-2 showed that the increase in specific surface area and total pore volume of the catalyst after impregnation Zr metal. The increase in specific surface area and total pore volume is expected because of the inclusion of Zr metal on the surface of the natural zeolite pores to form a new one. In this study obtained zeolite pore diameters increased after the impregnated metal. The effect of adding metal to the zeolites can also be seen from the average pore diameter also increased. The average diameter of the pores in the catalyst pores indicate the size of the microporous and mesoporous well used for the formation of short-chain hydrocarbons.

The acidity of the catalyst was tested with ammonia and pyridine [10]. The size of the ammonia molecule is smaller than the pyridine, so the ammonia gas can be adsorbed on the outer surface and within the zeolite while pyridine will be

TABLE-2
RESULTS OF THE MEASUREMENT OF THE SPECIFIC SURFACE AREA, MEAN PORE AND TOTAL PORE VOLUME OF THE CATALYSTS

Catalysts	Wide specific Surface (m^2/g)	Average pore sizes ($\text{\AA}$)	Pore volume (cc/g)
H/ZA	23.27	157.7	2.374×10^{-2}
Zr^{4+}/ZA (10 %)	23.38	163.8	2.544×10^{-2}
Zr^{4+}/ZA 1(0 %)	11.70	248.6	2.033×10^{-2}
Regeneration			

adsorbed on the outer surface of the zeolite. Qualitatively strength acid sites (acidity) can be determined for proton bonded to pyridine, namely the formation of the pyridinium ion prove Brønsted acidic.

Fig. 2 showed that differences in the IR spectra of the catalyst H/ZA and Zr^{4+}/ZA with the increase in uptake. Increased acid sites is possible because impregnated metal on the zeolite. Table-3 indicates a possible Zr metal carried cause an increase in the acidity of the catalyst as Zr metal d orbitals which have not been filled so effectively accepts an electron pair from a base adsorbate. The existence of a large number of active sites, the adsorption power of the reactants are also getting higher.

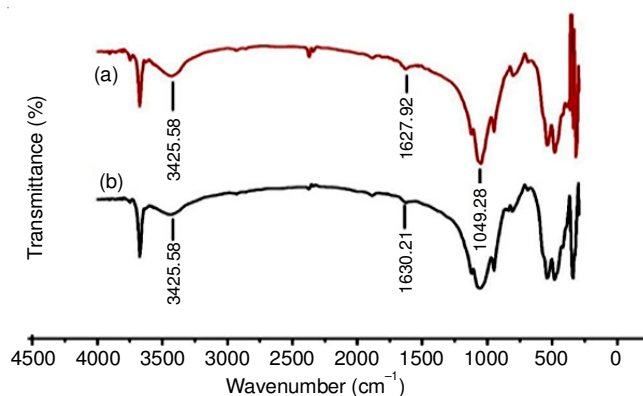


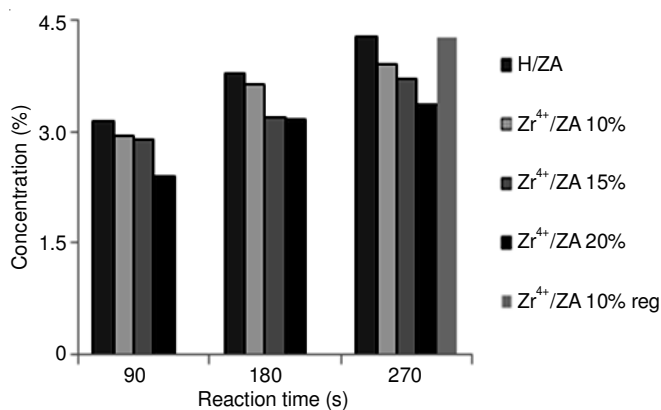
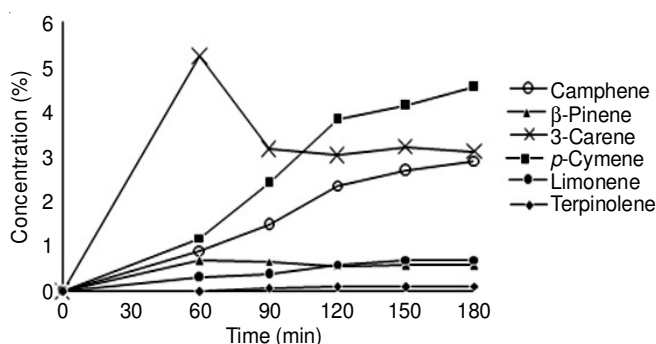
Fig. 2. IR spectra of H/ZA and Zr^{4+}/ZA catalysts

TABLE-3
RESULT OF DETERMINATION OF THE AMOUNT OF ACID CATALYST SITES

Catalytic	Acidity (mmol/g)	
	Total (ammonia)	Surface (pyridine)
H/ZA	2.76	0.10
Zr^{4+}/ZA	6.64	0.14

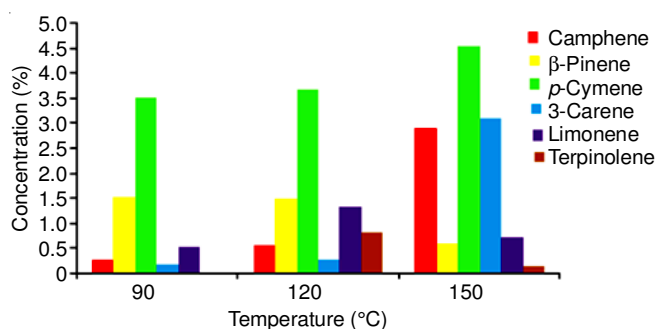
Fig. 3 showed that the greatest conversion of pinene used catalyst Zr^{4+}/ZA 10 %. The metal catalyst dropped on Zr^{4+}/ZA 10 % is the largest of the three catalysts used for the reaction. Effect of reaction time on the results of α -pinene isomerization reaction at 150°C are presented in Fig. 4. The produced isomer compounds were β -pinene, 3-carene, p -cymene, limonene and terpinolene. Camphene the largest concentration resulting from the reaction product with the catalyst Zr^{4+}/ZA 10 %. The highest conversion of α -pinene compounds in the reaction time of 180 min at 9.24 % with concentration of α -pinene 85.50 %.

Comelli *et al.* [6] conducted a α -pinene isomerization reaction with zirconium sulfate catalyst at a reaction temperature of 90 and 120°C , the product obtained isomer compounds

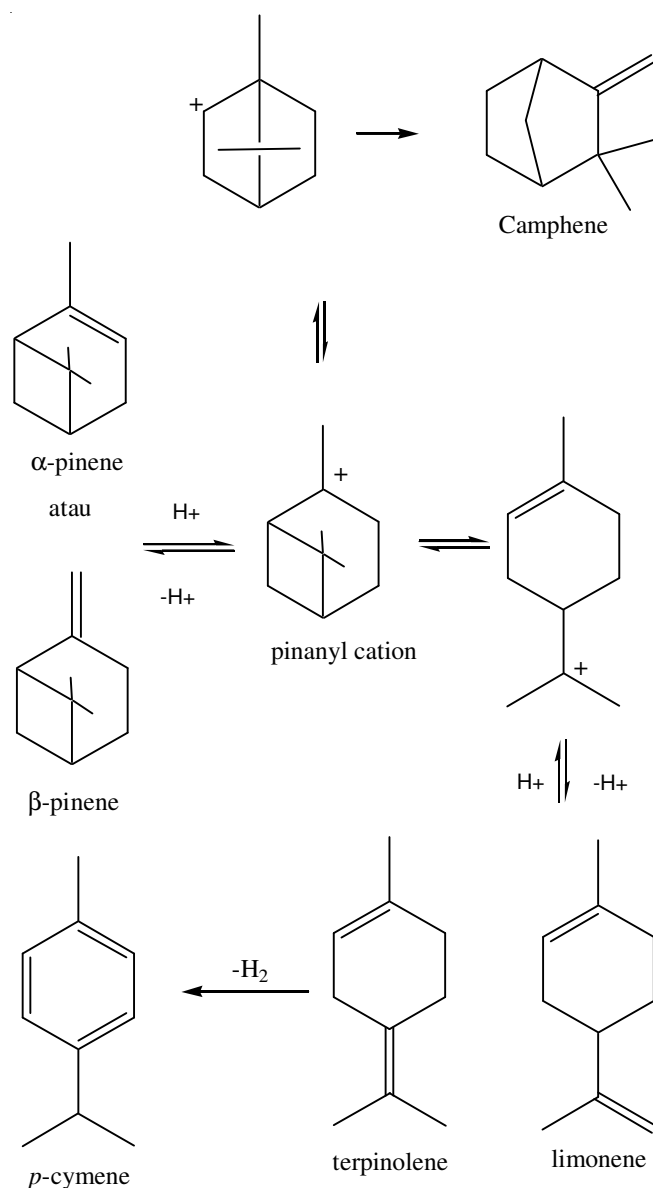
Fig. 3. The conversion α -pinene using H/ZA and Zr^{4+} /ZA catalystsFig. 4. Effect of reaction time on α -pinene isomerization. Catalysts Zr^{4+} /ZA 500 mg, 10 mL α -pinene temperature of 150 °C

include camphene, *p*-cymene, limonene and terpinolene with the largest concentration in the reaction time of 180 min.

The effect of temperature of the reaction on the conversion of α -pinene is shown in Fig. 5. Increasing the reaction temperature also increased the percent conversion of α -pinene. At a temperature sufficient conditions, provided sufficient energy so that the possibility of collision between the reactants that cause the reaction will be even greater, so that the resulting product will also increase [11]. Results of α -pinene isomerization reaction at each temperature variations produce increased levels of products with the increase in reaction time. There are many products that increased levels then declined at a certain reaction time. Compounds that increase levels and then decline is possible because in the course of the reaction to form other compounds (intermediates) are not isomers of α -pinene [5].

Fig. 5. Effect of temperature on concentration of product isomers. Catalyst Zr^{4+} /ZA 500 mg, 10 mL α -pinene, 30 min

The pathway for isomerization of α -pinene to monocyclic (limonene, terpinolene) and bicyclic (camphene) starts with the formation of pinanyl cation (Fig. 6). The *p*-cymene also formed from α -terpinene by the hydrogenation reaction [6].

Fig. 6. Scheme of α -pinene isomerization reaction

Conclusion

The isomerization of α -pinene catalyzed Zr^{4+} /natural zeolite is fast and lead mainly to monocyclic and bicyclic monoterpene. The reaction time and temperature effect on α -pinene conversion into isomers compound as indicated by the increasing concentration of isomer products. The optimum temperature and time reaction in this study was 150 °C and 180 min, respectively with the isomer forms are camphene, β -pinene, 3-carene, *p*-cymene, limonene and terpinolene.

ACKNOWLEDGEMENTS

The authors thank Directorate General of Higher Education (DGHE), Department of National Education Republic, Indonesia for its support.

REFERENCES

1. C. Catrinescu, C. Fernandes, P. Castilho and C. Breen, *Appl. Catal. A*, **489**, 171 (2015); <https://doi.org/10.1016/j.apcata.2014.10.028>.
2. N. Wijayati, H.D. Pranowo, J. Jumina and T. Triyono, *Indo. J. Chem.*, **13**, 59 (2013); <https://doi.org/10.22146/ijc.21327>.
3. B. Wiyono, S. Tachibana and D. Tinambuan, *Pak. J. Biol. Sci.*, **9**, 7 (2006); <https://doi.org/10.3923/pjbs.2006.7.14>.
4. J.-Y. Wang, P.-N. Wang, J. Yang, J. Shen, X. Xu and S.-F. Wang, *Asian J. Chem.*, **26**, 7779 (2014); <https://doi.org/10.14233/ajchem.2014.17781>.
5. N.A. Comelli, E.N. Ponzi and M.I. Ponzi, *J. Am. Oil Chem. Soc.*, **82**, 531 (2005); <https://doi.org/10.1007/s11746-005-1105-2>.
6. N.A. Comelli, E.N. Ponzi and M.I. Ponzi, *Chem. Eng. J.*, **117**, 93 (2006); <https://doi.org/10.1016/j.cej.2005.08.006>.
7. M. Yadav, C. Chudasama and R. Jasra, *J. Mol. Catal. Chem.*, **216**, 51 (2004); <https://doi.org/10.1016/j.molcata.2004.02.004>.
8. A. Severino, A. Esculcas, J. Rocha, J. Vital and L. Lobo, *Appl. Catal. A*, **142**, 255 (1996); [https://doi.org/10.1016/0926-860X\(96\)00091-9](https://doi.org/10.1016/0926-860X(96)00091-9).
9. L. Grzona, N. Comelli, O. Masini, E. Ponzi and M. Ponzi, *React. Kinet. Catal. Lett.*, **69**, 271 (2000); <https://doi.org/10.1023/A:1005643731718>.
10. A. Mara, K. Wijaya and W.T. Mudasir, *Asian J. Chem.*, **28**, 11 (2016); <https://doi.org/10.14233/ajchem.2016.19107>.
11. D. Santi, *ISTECH*, **5**, 104 (2013).