

PREPARATION AND MECHANISTIC STUDY OF ZnO/ZEOLITE AS CATALYST IN 1-PENTANOL DEHYDRATION

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ABSTRACT

Preparation of zinc oxide impregnated zeolite from natural zeolite and its catalytic activity in pentanol dehydration was investigated. The impregnation process was conducted by two main steps; chemical activation followed by wet impregnation using $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ as precursor and the characterization of prepared material was conducted by X-ray diffraction, scanning electron microscope (SEM-EDX) and surface acidity measured by pyridine adsorption-FTIR spectrophotometric method. As catalytic activity evaluation, pentanol dehydration over prepared material under vapor phase reaction mechanism was conducted by varied temperature of 300,400, 500 and 700°C. For mechanistic study, the product of reactions was analyzed by using gas chromatography-mass spectrometry(GC-MS). It is found that temperature affect strongly to the reaction mechanism in that at the temperature of above 500°C the etherification was occurred. From the comparison with zeolite, it can be noticed that the role of solid acidity also influences the reaction mechanism.

Keywords: Alcohol Dehydration, Natural Zeolite, Impregnatio, Heterogeneous Catalysis.

Introduction

Alcohol dehydration becomes one of important reaction in alternative energy development, for example the conversion of alcohol to ether. For the conversion, several solid acids have been reported to be successful in catalysing the reactions especially the catalyst with acidity and catalyst thermal stability as the important physical properties for the mechanism[1]. Silica alumina materials such as clay and modified clay as well as zeolite and its modified form have been previously reported. Zeolite with sufficient surface acidity, high specific surface area and higher thermal stability compared to clay is one of the silica alumina mineral for heterogeneous catalysis in alcohol dehydration. The presence of Lewis and Brønsted acid sites of zeolite that enhanced by thermal condition is the main reason which theoretically and practically proven. However, in order to improve the activity and selectivity towards a specified product, some modification regarding to the surface functionalization is required. Especially for natural zeolites as raw material in catalyst preparation, major drawback that has been discussed are mainly related with the poor thermal stability character and also their low tolerance to hot liquid water as product of dehydration[2][3]. Based on some researches on the utilization of zinc oxide and its composite forms as highly active in alcohol conversions, this investigation is efforted to improve catalytic properties of zeolite by impregnation of ZnO onto zeolite as solid support. Aim of research is to study on the change of physicochemical character in its relation with catalytic activity in 1-pentanol dehydration. Effect of the formation of ZnO in advance effect of temperature to the catalytic mechanism is discussed.

Materials and Method

The zeolite used as raw material in this research was natural zeolite obtained from Klaten, Jawa Tengah Indonesia. The powder of zeolite was chemically activated by refluxing in hydrochloric acid 0.1M for 6h followed by neutralization before using. Zinc acetate dihydrate ($ZnO \cdot 2H_2O$), ethanol, 1-pentanol were purchased from Merck-Millipore.

ZnO/zeolite catalyst was prepared by impregnation method. Precursor solution prepared from zinc acetate diluted in ethanol:water solvent was dispersed into zeolite powder slurry followed by stirring for a night. Solvent was then evaporated slowly before drying and calcined at 700°C for 5h. Powder of ZnO/Zeolite was characterized by x-ray diffraction (XRD) analysis collected using Shimadzu X6000 instrument, gas sorption analysis by NOVA1200e and surface acidity determination by pyridine adsorption-FTIR analysis. Sample in a desiccator was evacuated for 4h before exposed with pyridine vapor for a night and measured by using FTIR spectrophotometer after reevacuation for 1h. An AVATAR FTIR spectrophotometer instrument was utilized for this purpose. Pentanol as feed was vaporized before was purged into catalyst column at varied temperature. The temperature inside the reactor was controlled with a CAL 9500P controller (CAL Controls Ltd.). Product of reaction was condensed and the liquid was then analyzed using a GCMS instrument. Reaction parameters of catalyst activity, total conversion and product selectivity were calculated based on GCMS analysis by using following equation[4]:

$$\text{Total Conversion}(\%) = \frac{\text{mole of } [1 - \text{pentanol}]_i - [1 - \text{pentanol}]_p}{\text{mole of } [1 - \text{pentanol}]_i} \times 100\%$$

$$\text{Catalyst Activity}(\%) = \frac{\text{mole of } 1 - \text{pentanol reacted to form product}}{\text{mole of } 1 - \text{pentanol reacted}} \times 100\%$$

$$\text{Selectivity of product } i(\%) = \frac{\text{mole of } [Product - i]}{\text{mole of } 1 - \text{pentanol reacted}} \times 100\%$$

$[1 - \text{pentanol}]_o$, $[1 - \text{pentanol}]_p$ are peak area of 1-pentanol in feed and product respectively

Result and Discussion

Physicochemical character of catalyst plays role in the catalysis mechanism. As catalyst in alcohol dehydration, the presence of surface acidity and surface active sites will directly drives the interaction amongs reactants. Confirmation on the formation of crystalline and porous structure from the dispersion of ZnO on zeolite surface was observed by x-ray diffraction and Brunair-Emmet-Teller (BET) isotherm adsorption-desorption profile from gas sorption analysis. XRD pattern of both ZnO/zeolite and activated natural zeolite is depicted in Figure 1.

From the pattern it can be seen that there is no significant change in zeolite structure as shown by the relatively similar intensity of all reflections corresponding to the presence of zeolite structure. Some reflections at $2\theta = 9.89$; 27.58 ; and 29.80 are the indications for the mordenite structure and Clinoptilolite structure are confirmed by other reflections at : 22.43° [5]. Those reflections are appeared in ZnO/Zeolite pattern beside of the reflection related to the occurrence of ZnO phase at $2\theta = (2\theta)$ of 31.3670 , 34.0270 , 35.8596 correspond to the reflection from: 100,002, and 101 crystal planes, respectively (JCPDS card no.0-3-0888)[6], [7].

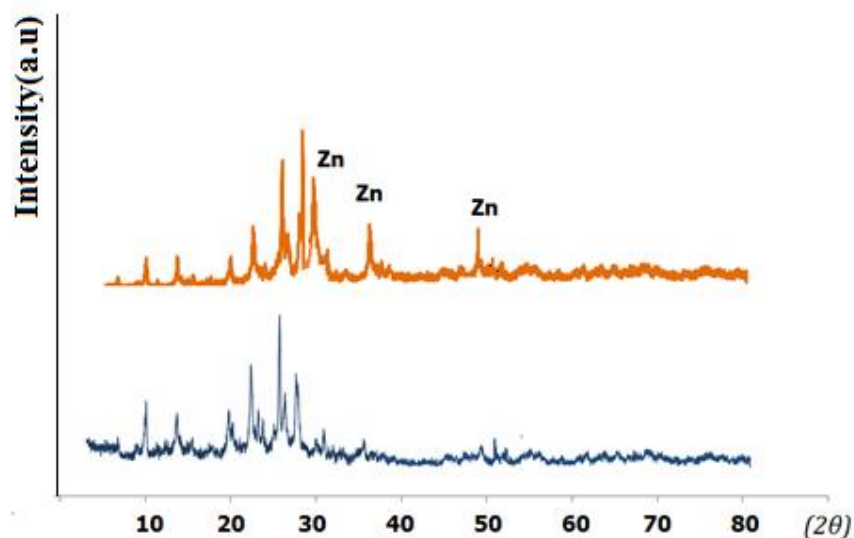


Figure 1. XRD Pattern of ZnO/Zeolite (above) and Zeolite (bellow)

ZnO impregnation also affects to the N₂ adsorption-desorption profile as presented in Figure 2 contribute to the specific surface area, pore volume and pore radius data listed in Table 1. Although was not significantly different, the adsorption capability of ZnO/zeolite is higher compared to zeolite as shown by the higher volume adsorbed at all P/P₀ condition. Pore distribution appeared in Figure 2(c) showed that ZnO/Zeolite has higher volume at all pore radius. From the calculation based on the adsorption with BET isotherm data, the higher specific surface area and pore volume were recorded (Table 1) while the pore radius of ZnO/Zeolite is lower than that of Zeolite. This is the indication of the ZnO aggregates formation on surfaces which tends to create aggregate pores.

Table 1. Surface Parameter from BET Surface Area Analysis of ZnO/Zeolite and Zeolite

Catalyst	Specific area(m ² /g)	Surface	Pore Radius (Å)	Pore volume (cc/g)
ZnO/Zeolite	80.67		12.21	38.56 x10 ⁻³
Zeolite	49.43		14.93	28.7x10 ⁻³

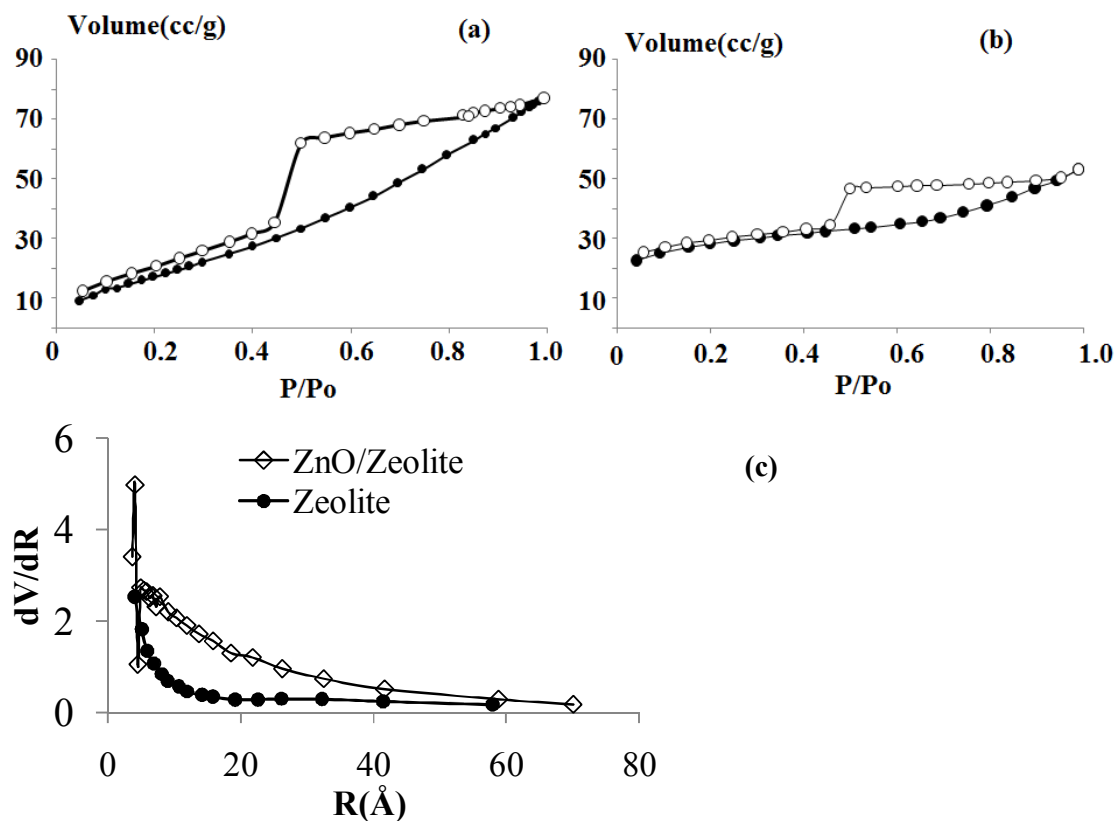


Figure 2. Adsorption-Desorption Profile of ZnO/Zeolite and Zeolite

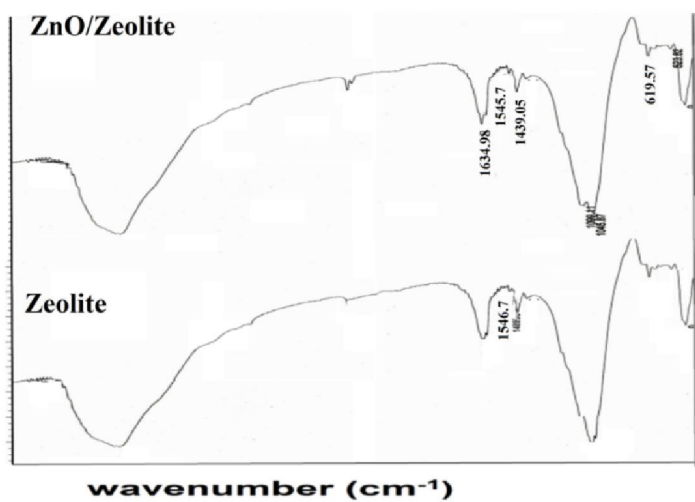


Figure 3. FTIR of ZnO/Zeolite and Zeolite after Pyridine Adsorption

Table 2. Total Acidity and Lewis to Broensted Acidity Ratio of ZnO/Zeolite and Zeolite

Sample	Acidity (mmol pyridine/g)	Total Acidity (mg butylamine/g)	L/B ratio
Activated Zeolite	0.460	0.775	0.99
ZnO/Zeolite	0.760	1.110	1.09

Catalytic activity of ionized zeolite is related to the presence of acid sites from tetrahedral $[AlO_4]^{5-}$ of zeolite framework in that these sites have character to be both Broensted and Lewis acid. Pyridine adsorption followed by FTIR analysis and also determination of total acidity by using n-butylamine titration were used to observed surface acidity qualitative and quantitatively. Analysis of surface acidity by using pyridine adsorption is based on the interaction between aromatic ring and nitrogen atom of pyridine. Aromatic ring of pyridine can bind to Broensted acid of H^+ and other protons from zeolite structure while nitrogen atom can coordinatively bind to Lewis acid sites i.e from Zn atom supported on surface. Spectra of FTIR is presented in Figure 3 and the data on total acidity and also Lewis to Broensted acidity ratio are compiled in Table 2.

Symmetrical bending of Al-O-Al and Si-O-Si are appeared at $650-720\text{ cm}^{-1}$ while absorbance at the region of $950-1250\text{ cm}^{-1}$ are correspond to asymmetric stretching. The interaction between adsorbed pyridine are indicated from some peaks at around 1450.52 cm^{-1} and 1546.72 cm^{-1} which correlated to the bonding between N of pyridine and proton (H^+) of zeolite. From the calculation based on FTIR spectra it can be noted that ZnO/Zeolite has higher total acidity and also L/B ratio. The insertion of zinc oxide particles are the main reason for the enhancement of acidity because of the contribution of d-orbitals of dispersed Zn. Lewis acid-base interaction comes from the bonding between electrone pairs of nitrogen to the formation Zn with coordination bonding.

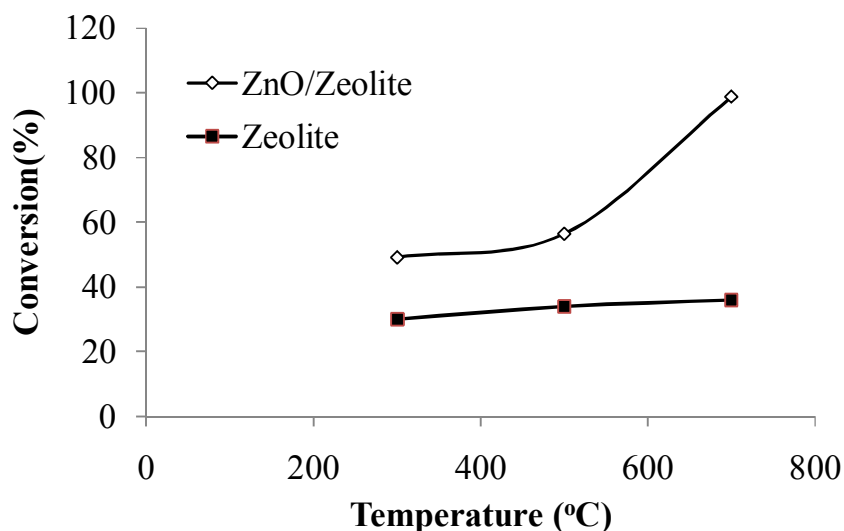


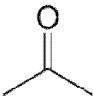


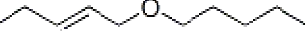


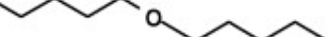

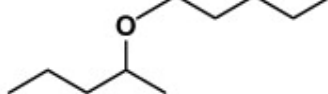
Figure 4. Effect of Temperature on Total Conversion

Catalytic activity test of prepared material showed that the total conversion increased withincreasing reaction temperature(Figure 4). Furthermore, ZnO/Zeolite exhibited a higher

conversion at all reaction temperatures, reaching complete conversion at 700 °C compared with zeolite. In advance analysis of converted products catalyzed by ZnO/Zeolite were determined by using GCMS analysis as listed in Table 3. It can be seen that at 400°C the product consisted of 2-pentanone which is also produced over activated zeolite at all temperature condition. The yield was gradually changed with increasing temperature whereas at 500°C and 700°C the product of 1-pentyloxy pentene was formed. The product was observed only over ZnO/Zeolite which indicate the role of ZnO as active sites in the catalysis mechanism.

At relative low temperature (400°C) thermal effect seems occurred since the product of 2-propanone was found. The route of conversion probably consist of thermal cracking to produce ethylene gas and followed by oxidation to produce 2-propanone. The domination of thermal effect compared to catalytic effect may related to that catalyst was in the inactive condition. As the temperature increased, the product of 1-pentyloxy-2-pentene, penten-1-yl, pent-2-yl ether and di-n-pentyl ether were produced and gradually enhanced by higher temperature. The mechanism of etherification within the dehydration was dominantly occurred within both varied temperatures. The possible mechanism occurs is presented in schematic mechanism as modified from [8].

Table 3. Product of 1-pentanol dehydration over ZnO/Zeolite at varied temperature

Temperature	Product of Reaction	Structure	%
400°C	2-propanone		48.75
	1-pentanol		50.81
	2-pentanone		0.15
500°C	1-pentanol		43.55
	1-pentyloxy-2 pentene		11.46
	Pentanoic acid		0.28
	Heptane		0.58
700°C	1-pentanol		1.24
	Di n-pentil ether		21.26
	1-pentyloxy-2 pentene		7.98
	penten-1-yl, pent-2-yl ether		8.10

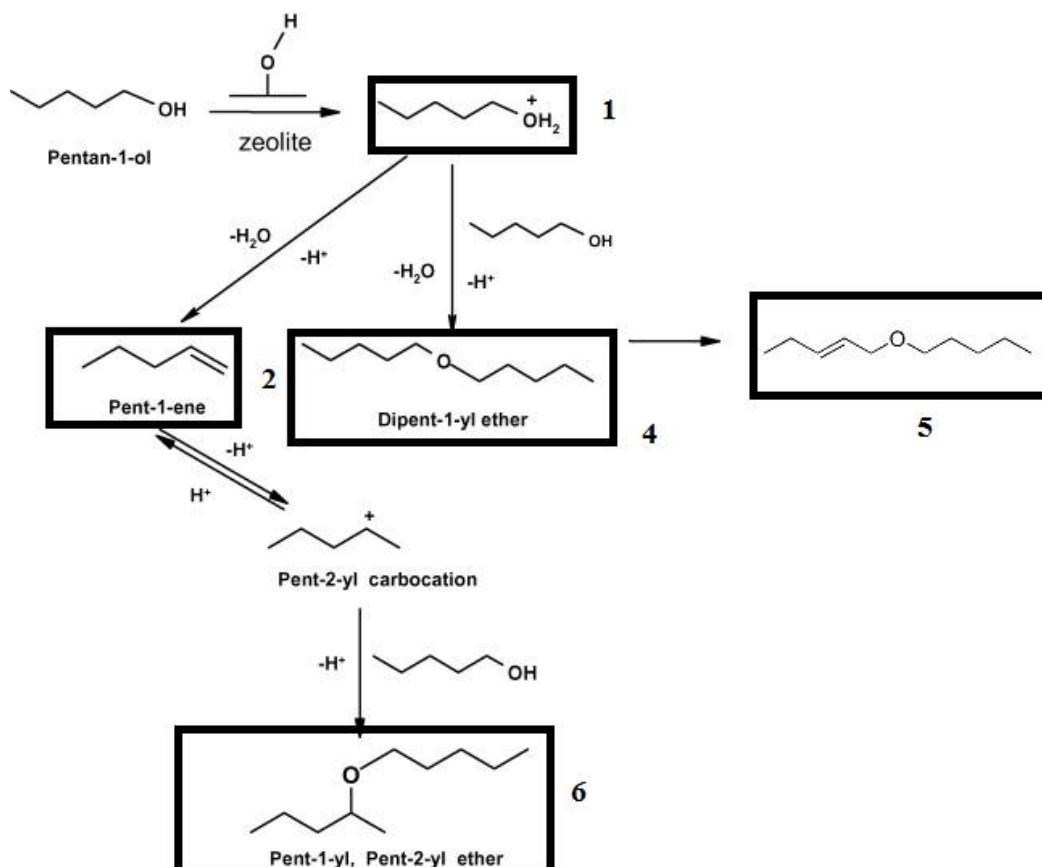


Figure 5. Schematic Possible Mechanism of 1-pentanol Dehydration as modified from Mohammed and El-Esaimi[8]

1-pentyloxy-2-pentene(5) is probably produced from the bimolecular interaction between pent-1-ene(2) and carbocation (1). The ionic interaction has higher possibility and theoretically enhanced since the surface active of Zn on zeolite surface active[4]. The possible route for the formation of this compound attribute to the strong adsorption of intermediate product(1) and (2) by the surface leads to the structural rearrangement to form the compound(4). It is also showed by the presence of heptane as a result as well as propanoic acid. At higher reaction temperature of 700°C, it can be seen that penten-1-yl, pent-2-yl ether(6) and di-n-pentyl ether(4) were produced. The product of (4) is the main chemical targetted in this mechanism as reported by several authors [4], [8], [9] while the product (5) was similar compound that was also reported from the 1-pentanol dehydration over zeolite[8]. From elucidating the mechanism it can be concluded that ZnO impregnation onto zeolite surface contributes significantly to the surface activity and that is strongly correlated to the surface acidity improvement.

Conclusion

In this research ZnO/Zeolite has been succesfully prepared with enhanced physicochemical character that support the function of the material as catalyst for 1-pentanol

dehydration. An important character of surface acidity presents the active sites in the catalysis mechanism. An important concept presented from the varied temperature is that surface active properties of ZnO/Zeolite affects the mechanism involved via the adsorption of reactant by Zn metal dispersed on solid support. Bimolecular interaction on surface occurs at the temperature 500°C and 700°C while at 400°C thermal effect is relatively dominant.

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