ADSORPTION ISOTHERM OF ETHANOL AND WATER IN GAS PHASE ON ZEOLITE A

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ABSTRACT

Wuntu, A. and M. Kumaunang, 2009. Adsorpsi Isoterm dari etanol dan Air dalam fase gas pada zeolit A.

Isoterm adsorpsi air dan etanol fase gas pada zeolit A yang disintesis dari silika gel dan aluminium hidroksida serta diaktivasi pada 373 K dan 573 K telah dikaji. Eksperimen dilakukan menggunakan metode gravimetri pada kondisi statis dan data yang diperoleh dianalisis menggunakan model isoterm adsorpsi Dubinin-Raduskevich untuk memperoleh nilai kapasitas adsorpsi dan energi adsorpsi. Hasil yang diperoleh menunjukkan bahwa kapasitas adsorpsi zeolit untuk air lebih besar dibandingkan untuk etanol karena molekul air berukuran lebih kecil dan lebih polar. Suhu aktivasi zeolit yang tinggi mengakibatkan energi adsorpsi zeolit untuk air dan etanol menjadi lebih kecil.

Keywords : adsorpsi, isotherm, zeolit

INTRODUCTION

Zeolite A is one of the synthetic zeolite and is first synthesized and described by Milton (1959) in a hydrothermal condition. At present, zeolite A is used in various industrial application, especially as a catalyst and desiccant and in the field of purification. The reasons for its wide application lie on its specific properties as an adsorbent which related to its porous structure and Si/Al ratio of 1 to 3.5. The porous structure of zeolite A with pore diameter of about 4 Å makes the small molecules only, such as water, to enter its cavities. On the other hand, small Si/Al ratio creates the zeolite as a polar adsorbent which tends to adsorb polar molecules such as water.

Many aspects have been studied by many researchers regarding the synthesis of zeolite A. One of the aspects is the use of various raw materials in zeolite A synthesis. Tuff (Donevska, 1985; Stamboliev *et al.*, 1985), fly ash waste (Stamboliev *et al.*, 1985), halloysite and allophane (Wolff and Meyer, 2005), and rice husk ash (Nur, 2001) are examples of starting materials that can be used in the synthesis. Wuntu (2002) had synthesized zeolite A using silica gel and aluminum hydroxide in a simple procedure. Its properties, however, are not well studied, especially its adsorption properties for molecules in gas phase. This paper describes the adsorption properties of the zeolite for water and ethanol molecules in gas phase. It is possible to expand the experiment to other substances such as volatile organic compounds which are common in closed indoor space.

METHODOLOGY

Zeolite A used in this research obtained by synthesis according to procedure described by Wuntu (2002) with hydrothermal condition of 363 K for four hours. Adsorption isotherm of water and ethanol in gas phase is then determined using gravimetric method in static condition. About one gram of the zeolite activated at 373 K for one hour is placed inside a 5 L plastic container along with 0.10, 0.08, 0.06, 0.04, or 0.02 mL water. The system is then stayed for 24 hours prior to the recording of the increasing weight of the zeolite. The similar procedure is performed for ethanol of the same volume and the whole procedure is repeated using zeolite activated at 573 K for four hours. Data gained is analyzed according to Dubinin-Raduskevich (DR) adsorption isotherm model which can be used to calculate the adsorption capacity and adsorption energy. DR equation is expressed in the form of:

 $\ln W = \ln W_o - [1/(\beta E_o)]^2 [RT \ln(P_o/P)]^2$

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where W is adsorbate volume in micropore at temperature T, W_o is total volume of micropore, R is gas constant, P_o is saturated vapor pressure of adsorbate at temperature T, P is partial pressure of adsorbate, β is coefficient of affinity, and E_o is adsorption energy. If the adsorption follows DR equation then plot of W vs. $[\text{RT } \ln(P_o/P)]^2$ would

generate a straight line specific for the adsorbent with intercept ln W_o and slope $[1/(\beta E_o)]^2$.

RESULTS AND DISCUSSION

Adsorption of water and ethanol in gas phase on zeolite A activated at 373 K and 573 K according to DR adsorption isotherm model are presented in Figure 1.

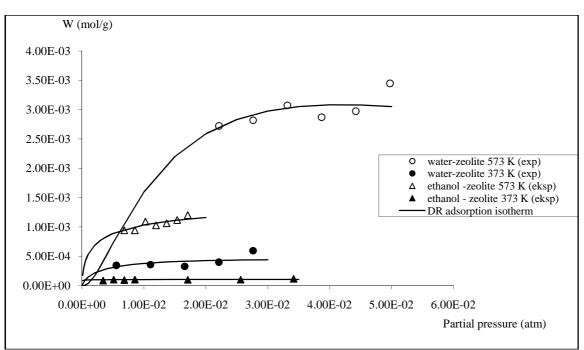


Figure 1. Adsorption isotherm of water and ethanol on zeolite A

Isotherm curves in Figure 1 qualitatively show the difference between the adsorption of water and ethanol and between zeolite activated at 373 K and 573 K. Water and ethanol adsorptions are quantified using DR parameters (Table 1) determined from DR equation for adsorption capacity and energy.

Adsorbent	Parameter	Zeolite A (373 K, 1 hour)	Zeolite A (573 K, 4 hour)
Water	W ₀ (mol/g)	4.43×10^{-4}	3.08×10^{-3}
	E ₀ (kJ/mol)	27.01	13.48
	β	0.33 *	0.33 *
	\mathbf{R}^2	0.2806	0.3642
Ethanol	$W_0 (mol/g)$	$1.11 \text{x} 10^{-4}$	1.37×10^{-3}
	E ₀ (kJ/mol)	23.38	13.79
	β	0.79 *	0.79 *
	\mathbb{R}^2	0.5953	0.786

* affinity coefficient of acetone = 1

Table 1 shows that zeolite A activated at 373 K has smaller adsorption capacity than that

activated at 573 K as showed by the value of W_0 . Activating zeolite at high temperature is aimed to drive out unwanted contaminant adsorbed on surface of zeolite and to provide surface for water and ethanol adsorption. The higher the activation temperature, the more contaminant could be expelled and the higher the adsorption capacity. In relation to activation temperature, Milton (1959) stated that the amount of water that could be adsorbed by zeolite A depends on activation temperature and that zeolite A could be activated up to 600 °C. At higher temperature zeolite A could be decomposed.

Data in Table 1 also shows that the adsorption capacity for water is higher than that for ethanol at each activation temperature. The result could be explained in two ways. Firstly, the size of water molecule is much smaller than that of ethanol molecule and the water, consequently, has greater freedom to pass through the pore of zeolite A (Figure 2). Although the size of the molecules showed in Figure 2 are smaller than the size of the pore of zeolite A, kinetics diameter of the molecules are much higher and ethanol molecule, therefore, has lesser possibility to enter the cavity inside zeolite framework. Water, for instance, has the size of 1.536 Å that is smaller than its kinetics diameter of 2.65 Å (SEMCO Inc., 2005). Secondly, the polar zeolite A tends to adsorb water molecule that is more polar than ethanol molecule. Higher aluminum content in zeolite A makes zeolite A a polar adsorbent for Al-O-Al in zeolite framework has greater ionic character than Si-O-Si. Selective properties of zeolite A for polar molecules has stated by Milton (1959) that patented the method of synthesizing and activating synthetic adsorbent of crystalline sodium aluminum silicate.

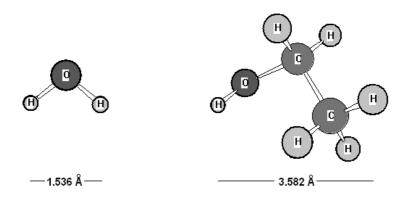


Figure 2. Comparison of the size of water and ethanol molecules

Calculation using DR equation shows that the energy adsorption of water is relatively the same as that of ethanol on zeolite A for each activation temperature. On the other hand, the energy adsorption of water or ethanol on zeolite A activated at 573 K is lower than that activated at 373 K (Table 1). In accordance with the Theory of Volume Filling of Micropores (TVFM), the size of micropore in adsorbent could be changed by activation, which is the longer the activation time at high temperature the larger the pore size. Carrot et al. in Cal (1995) stated that the slits or pores with smaller widths are characterized having the greatest adsorption energy due to the superposition of the adsorption potentials of opposite pore walls. It is reasonable, then, that water and ethanol are adsorbed stronger on zeolite A activated at lower temperature than that activated at higher one.

CONCLUSIONS

It could be concluded that the adsorption properties of water and ethanol on zeolite A synthesized from silica gel and aluminum hydroxide depend on the properties of water and ethanol and of the zeolite which affected by activation temperature. The amount of the smaller and more polar water molecule adsorbed on zeolite is larger than that of the larger and less polar ethanol molecule. Activation temperature could affect the adsorption capacity and energy. The higher the activation temperature, the greater the adsorption capacity, while zeolite A activated on 373 K adsorbs water and ethanol stronger than that activated on 573 K.

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