

PRELIMINARY STUDY OF SIMULATION FOR ILLUSTRATING DEHYDRATION PROCESS OF BIOETHANOL TO DIETHYL ETHER USING SUZ-4 ZEOLITE CATALYST

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Abstract

Process simulation for catalytic dehydration of bioethanol to diethyl ether or DEE over SUZ-4 zeolite catalyst was constructed from a canonical Monte Carlo Simulation. The position of SUZ-4 zeolite structure was designed by Wyckoff positions of group 65 (*Cmmm*). The SUZ-4 zeolite framework consists of connected $K_4Al_4Si_{32}O_{72}$, which has an orthorhombic crystal structure. The length of unit cell is $a = 18.8064 \text{ \AA}$, $b = 14.2298 \text{ \AA}$, and $c = 7.4548 \text{ \AA}$. DEE can be used as the alternative fuel for diesel engine due to its low auto-ignition temperature and high Cetane number. Thus, this work aims to convert bioethanol to DEE for this purpose. DEE is produced by the dehydration of ethanol which is an endothermic reaction that requires heat and catalysts. This reaction occurs in the vapor phase at a temperature between 150 and 300°C. The simulation results found that the increase of the double amount of bioethanol gave a %ethanol conversion increasing of 2-3%. While the increase of %active site within 60-100% provided %ethanol conversion rising of 40%-80%. The probability of a catalytic dehydration process of the active site position found that the ethanol molecules of the active site in 8-membered rings and 10-membered rings can be accessed more than the 6-membered rings.

Keywords: Catalyst, zeolite, SUZ-4, adsorption

Introduction

Zeolites are crystalline aluminosilicates of group IA and group IIA elements, such as sodium, potassium, magnesium, and calcium (Breck, 1974). Chemically, this empirical formula of zeolite can be represented in general as follows: $M_{2/n}O \cdot Al_2O_3 \cdot ySiO_2 \cdot wH_2O$, where M is cations, y is the value is a range of 2-200, n is the cation's valence, w is the water content in the voids of the zeolite (Wilson, 2010). Zeolites are porous solids with the distribution of pores in the range of 0.3-2.0 nm in diameter. This is dependent

on its crystalline frameworks. Porous materials can be categorized according to pore width by the International Union of Pure and Applied Chemistry (IUPAC) are microporous material (pore diameter $\leq 2.0 \text{ nm}$), mesoporous material ($2.0 \text{ nm} < \text{pore diameter} \leq 50 \text{ nm}$), and macroporous material (pore diameter $> 50 \text{ nm}$). Thus, most of the zeolites are generally classified in a group of microporous materials. The frameworks of zeolites are composed of TO_4 tetrahedral ($T = \text{Si, Al}$) with O atoms

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connecting neighboring tetrahedral, which corner-share to form different structures. There are many species of zeolite minerals depend on crystalline frameworks. The most important property of zeolites with respect to their use as catalysts is their surface acidity (Weitkamp, 2000). Acid site or a Brønsted acid is an isomorphous substitution of Si by Al in the framework. Replacing Si with Al gives rise to a negative charge of the framework. Location of the catalytically active sites occur on the external surface of the crystal extent do the sites occur in large cavities, which are accessible for bulky reactant molecules. Acid sites evenly distribute over the crystals, or they are concentrated in a shell near the external surface or, conversely, in the core of the crystals. Catalysis is one of the important fields of application of zeolites (Weitkamp, 2000). SUZ-4 zeolite or Sunbury zeolite-four (SZR) is an originally synthetic zeolite patented by Barri, British Petroleum Company in 1992 (Barri, 1992). Its structure framework consists of five-, six-, eight-, and ten-membered rings according to Lawton (1993). The pore system of this zeolite includes straight ten-membered ring channels and small cages linked through the double six-membered rings. The minimum and maximum dimensions of the ten-membered rings are 4.1 Å and 5.2 Å, respectively, which are very like those in zeolite type ferrierite (Baerlocher *et al.*, 2001). The major difference between SUZ-4 and ferrierite is the alignment of these chains along the c-axis and SUZ-4 zeolite has 8-ring channels as well as 10-ring channels. SUZ-4 zeolite has the maximum diameter of a sphere that can be included in the channels (6.27 Å). Lukyanov *et al.* (1999) studied the acidic and catalytic properties of SUZ-4 zeolite indicated that the SUZ-4 zeolite has potential as a catalyst that may display unusual shape-selective properties in comparison with other zeolites.

Usually, ethanol catalytic dehydration is an endothermic reaction that requires heat and acid catalyst. This reaction occurs in the vapor phase in a fixed bed or fluidized bed reactor at a temperature range between 240°C and 450°C, depending on the type of catalyst (Kagyrmánova *et al.*, 2011).

The interests in the production of diethyl ether or DEE from ethanol are further studied about the improvement of the process or developing a new catalyst. Kamsuwan *et al.* (2017) studied the catalytic dehydration of ethanol over H-beta zeolite (HBZ) catalyst with ruthenium (Ru-HBZ) and platinum (Pt-HBZ) modification to increase the DEE yield at a low temperature. Taís Klein *et al.* (2018) focused on the dehydration of ethanol over the Cu-Fe/ZSM-5 catalyst and its influence on the selectivity of DEE.

Thus, this research was aimed to present the simulation of SUZ-4 zeolite structure and to study the factors that affected the catalytic dehydration process efficiency of ethanol to diethyl ether by SUZ-4 zeolite catalyst by Monte Carlo Simulation.

Methods

Simulation Method

The simulation method presented here follows the experimental steps to generate SUZ-4 zeolite and understand the dehydration process. SUZ-4 zeolite was synthesized by the sol-gel technique, followed by the hydrothermal process. Once the SUZ-4 zeolite is obtained, it is characterized for structural properties. In the case of the SUZ-4 zeolite, this is usually done with XRD techniques. In reaction part, to study the variation of ethanol to agree with experimental in terms of increasing and decreasing the concentration of ethanol, and varying the amount of active site. In case of deactivated after being used for a period of time. These results of the reaction shown in terms of % ethanol conversion. The summary of our procedure is shown in Figure 1. The following is the detailed description of the proposed method, which is divided into two sections, simulation method, and creation of SUZ-4 zeolite structure.

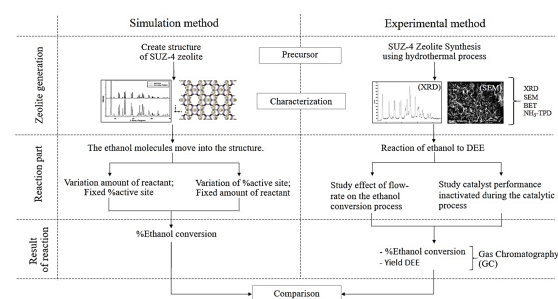


Figure 1. Schematic diagram to obtain and characterize a molecular model of the reaction of ethanol to DEE and the comparison with the experimental method

The simulation of the dehydration process in SUZ-4 Zeolite is generated to understand the dehydration process generally. The simulation is conducted based on the Monte Carlo Simulation. Firstly, the SUZ-4 zeolite was constructed as a simulated structure, as shown in Figure 2 an initial configuration to assign the initial positions of the active site on the zeolite structure. The other initial configuration is generated by the ethanol molecules and randomly place them in the bulk phase by using

a random number generator. The simulated reaction was started by randomly chosen two ethanol molecules and randomly moved to a new trial position (x' , y' , z'). If these molecules would overlap another molecule in the new position, then the new move was rejected, and the previous configuration was retained. If the new position of two ethanol molecules close enough to the active site, the two ethanol molecules at the active site were changed to one molecule of diethyl ether and H_2O , then these two product molecules were moved out from the system. The steps of the simulation process can be clearly seen in Figure 2.

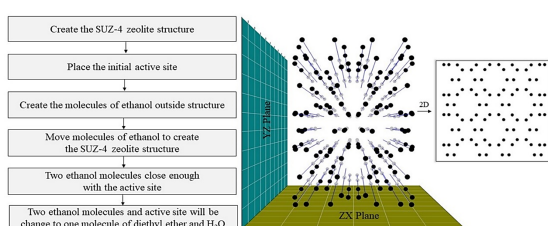


Figure 2. The steps of the simulation process and structure from simulated

Creation of SUZ-4 zeolite structure

This study created SUZ-4 zeolite structure simulated by using Wyckoff positions of group 65 (*Cmmm*) and Crystal chemical data of SUZ-4 or SZR zeolite structure is $K_4Al_4Si_{32}O_{72}$ orthorhombic with the length of the unit cell $a = 18.8064\text{\AA}$, $b = 14.2298\text{\AA}$, $c = 7.4548\text{\AA}$ (Baerlocher *et al.*, 2001). The proposed model of the framework topology was subjected to a constrained distance and angle least-squares (DLS) refinement. In these refinements, the prescribed T-O, O-O, and T-T distances were optimized at $1.62\text{\AA}$, $2.65\text{\AA}$, and $3.09\text{\AA}$, respectively. The refined atomic coordinates are listed in Table 1.

Simulation Process in the Part of the Reaction

For the first case of variation of ethanol in the reaction started from the reactants or ethanol loaded into the SUZ-4 structure that were randomly positioned. Then the cut-off radius was performed using the active site position as the origin point of the reaction for the %Ethanol conversion calculation. Cut-off radius is considered for the molecules of ethanol surrounding the active site, it is a sphere of the radius equal to $4.47\text{\AA}$, if those molecules are outside this sphere would not be accounted. For the second of the variation of active sites, a constant amount of ethanol molecules is loaded into structure with variation amount of active site. This does not mean that the ethanol molecules were previously existed. Then the calculation of

%Ethanol conversion was performed as earlier mentioned.

The dehydration process on acid catalysts takes place on the Brønsted acid site, the Lewis acid sites being inactive (Corma *et al.*, 1987). However, no information is available on Al-location in SUZ-4 zeolite for determining the Brønsted acid site. Therefore, this work is not being delved into the real structure of the SUZ-4 zeolite, but only to illustrate the process of ethanol dehydration to DEE. Consequently, we assumed the active site located at the potassium surface to investigate the possibility of a reaction and called that position an “active site” in order to avoid the misunderstanding that these sites are the real acid sites.

Table 1. Atomic coordinates for the proposed model of SUZ-4 from (Strohmeier *et al.*, 2006)

Atom	Position	X	Y	Z
T1	16r	0.0818	0.1976	0.2926
T2	8o	0.1463	0.00	0.2905
T3	4g	0.2677	0.00	0.00
T4	8p	0.1726	0.2974	0.00
O1	8n	0.00	0.2209	0.2449
O2	16r	0.0995	0.0916	0.2387
O3	8o	0.2195	0.00	0.1796
O4	4e	0.25	0.25	0.00
O5	8p	0.3196	0.0906	0.00
O6	16r	0.1309	0.2683	0.1811
O7	4h	0.1677	0.00	0.50
O8	8q	0.0992	0.2173	0.50

Results and Discussion

SUZ-4 Zeolite Structure and Active Site Position

The SUZ-4 zeolite in Figures 3(a) and 3(b) is composed of silicon 32 atoms, aluminium 4 atoms, oxygen 72 atoms, and potassium 14 atoms for 1 unit cell. The structure framework consists of small cage six-, eight-, and ten-membered rings. The results of the active site position were plotted in simulation in Figures 3(c) and 3(d) and illustrate active site position in pore systems were plotted only one cage along c is drawn for clarity. Chains of potassium atoms (yellow atoms) are parallel to b axis Figure 3(e).

The structure from this simulation of SUZ-4 zeolite conforms to the originally proposed *Cmmm* framework of Lawton (1993) and the XRD pattern of simulation compare with a database (Baerlocher and McCusker, 2013) of SUZ-4 zeolite structure in Figure 4, which confirm that all diffraction peaks that occur consistent with the details of a database. Moreover, the result is supported by the comparison of the experimental data with the XRD standard pattern of SUZ-4 zeolite (Price, 2001) at the

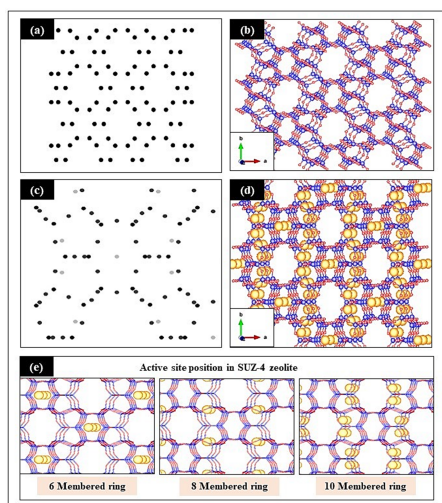


Figure 3. Illustration of the structure and pore systems of SUZ-4 zeolite from simulation viewed along C (The yellow color represents the active site of the structure). (a) and (b) The SUZ-4 zeolite structure, (c) and (d) Active site position. (e) Active site position in the pore systems

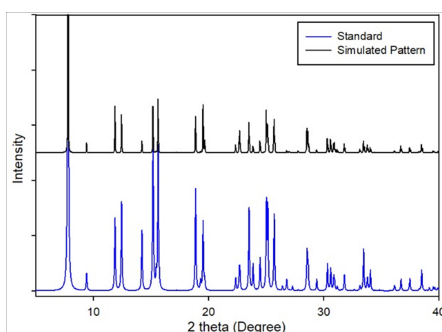
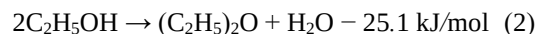
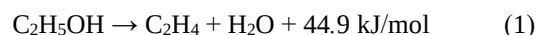


Figure 4. XRD patterns of SUZ-4 zeolite and calculated patterns of the hypothetical model, based on Cu-K α radiation. XRD pattern from SUZ-4 zeolite from database of zeolite structures (Baerlocher and McCusker 2013) and XRD pattern from simulated

following 2 θ positions; 7.7°, 11.8°, 15.1°, 19.3°, 24.8°, 25.5°, and 28.4°. While the intensity peak differences may be due to the presence of potassium in the structure (Lawton, 1993).

Process Simulation Result of the Catalytic Dehydration Reaction of Bioethanol to Diethyl Ether

In general, conversion of ethanol dehydration reaction can produce ethylene and diethyl ether in 2 competitive pathways as follows:



The reaction1 is an endothermic reaction and favors the moderate to the high temperature between 320°C and 500°C; in contrast, reaction2 is an exothermic reaction and favors the low to moderate temperature between 150°C and 300°C (Phung and Busca, 2015; Chong *et al.*, 2017; Anchale *et al.*, 2019). The %ethanol conversion was defined as follows:

$$X_{\text{EtOH}} = \frac{n_{\text{EtOH(A)}} - n_{\text{EtOH(B)}}}{n_{\text{EtOH(A)}}} \times 100 \quad (3)$$

where $n_{\text{EtOH(A)}}$ and $n_{\text{EtOH(B)}}$ are defined as the molar of ethanol in feed and ethanol do not adsorb with the active site, respectively. Considering the case of ethanol conversion, the ethanol can be converted into many products. The generated product depends on the condition such as high temperature would affect ethylene formation, and low temperature would give DEE as above mentioned. Therefore, this work is assumed the product of a reaction to be only DEE. Consequently, the ethanol conversion refers to the yield of DEE (Y_{DEE}). This work considered simulation result consists of two main parts are variation of reactant amount and variation of %active site.

Variation Amount of Reactant; Fixed %Active Site

The result of the variation amount of reactant and fixed %active site. When increasing the amount of ethanol, %ethanol conversion is around 80-85% and increase 3-5% when the double amount of ethanol content in the structure. Figure 5 shows a molecular model simulated before and after the reaction. Figure 5(b) represents input ethanol lower than Figure 5(d). The result found that when the passed of reaction change ethanol to DEE, some molecule ethanol was still in the structure owing to these atoms are not reactive with the active site Figures 5(c) and 5(d). However, the increase in ethanol content exceeds the existing active site position in the structure. This may cause some ethanol not adsorption at the active site location in order to cause a reaction. Another effect that affects the reduction of the reaction is the duration of use of the catalyst. The report from the experimental was found that the efficiency of the %ethanol conversion decreased by approximately 15.24% when the reaction passed over 65 h because the reaction polymerization of alkenes or hydrocarbon transformations is mainly owing to the deposit

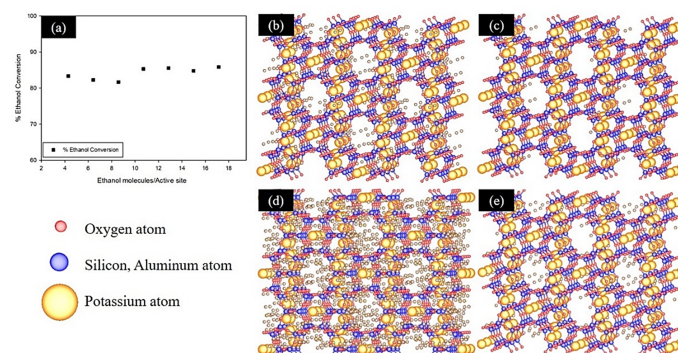


Figure 5. The result variation of reactant amount; fixed active site

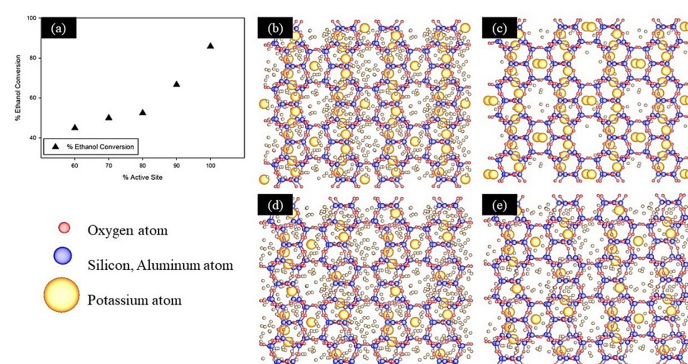


Figure 6. The result variation of active site; fixed reactant amount

inside the pores of secondary products generally known as coke, which the rate of coking and the deactivating effect of the coke molecules are an effect on the pore structure and the acidity of the zeolites as well as by the operating conditions (Guisnet *et al.*, 1997).

Variation of %Active Site; Fixed Amount of Reactant

The result of variation of the active site is found that %ethanol conversion tended to increase when increasing amount of active site Figure 6(b) is 100% active site in structure, while Figure 6(d) is 60% active site in structure. After the reaction ethanol was still in the structure of (Figure 6(e)) more than Figure 6(c) have full active site in structure caused by the atom ethanol is too far from the active site. This important finding demonstrates the effect of the number of acid sites on the formation of DEE. In addition, Anchale *et al.* (2019) reported that the factor to increase the ethylene and DEE selectivity is the amount of weak acid or Brønsted acid, which is the active site for ethanol dehydration. Besides, Thitipob Sirisoontornpanit *et al.* (2017) reported that the chemical surface

property of SUZ-4 zeolite was weak acid sites. While Taís Klein *et al.* (2018) found the strength of the surface acid sites from TPD-NH₃ results, the formation of DEE is favored by the presence of a medium in strength acid sites at low temperature.

The Probability of Dehydration Process at Active Site Position

The simulated reaction was started by randomly chosen ethanol molecules afterward randomly moved to the structure as shown in (Figure 7). The ethanol position was indicated the probability of ethanol conversion use cut-off radius around 4.47 Å for computed in this step, which cut-off radius compare with the results of catalytic conversion experiments of ethanol over the ferrierite zeolite catalysts (Phung *et al.*, 2015).

The probability of dehydration process at the active site position in the pore systems is presented in (Table 2). It can be observed that the small cage 6-membered ring. There is a low probability that is formed with ethanol in a reaction, previously Lukyanov *et al.* (1999) studied acidic and catalytic properties of SUZ-4 zeolite reported that SUZ-4 zeolite non-exchangeable hydrogen with potassium

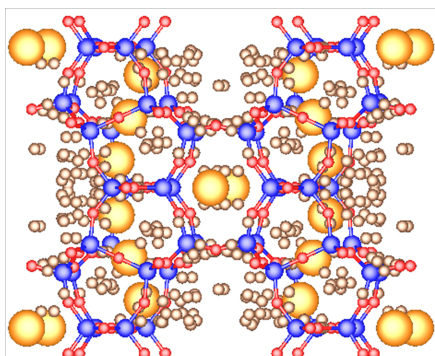


Figure 7. The distribution of ethanol molecules after moved into SUZ-4 zeolite structure

Table 2. The probability of dehydration process at the active site position in the pore systems

6-Membered ring	8-Membered ring	10-Membered ring
6.1812%	35.7405%	58.0783%

cations in small cages and/or in double six-membered rings which are present in SUZ-4 zeolite (Lukyanov *et al.*, 1999). Shewangizaw Teketel *et al.* (Teketel *et al.*, 2015) have reported that some of the acid sites in SUZ-4 zeolite are inaccessible, that some of the acid sites are located too closely to easy accommodation of molecules on every site, or that some of the sites are too weakly acidic to formed react together. Lawton (1993) have reported that only about 47% of the potassium cations were ammonium exchange and calcination, whereas Zholobenko *et al.* (1998) studied H-D exchange of SUZ-4 zeolite by used FTIR characterization technique found that in three IR bands at 3,560, 3,592, and 3,610 cm^{-1} corresponding to OH groups in 6-, 8-, and 10-membered rings. The intensity of the first band at 3,560 cm^{-1} is considerably low-intensity indicating that the residual potassium cations are located in small cages or in double 6-membered rings. This result showed that 8- and 10-membered rings have the chance of reactions more than 6-membered rings may be cause of the larger pores and number of active sites in a cage system.

Conclusions

The molecular structure of SUZ-4 zeolite is simulated by Wyckoff positions of group 65 (*Cmmm*). The increasing of the double amount of bioethanol gave % Ethanol conversion increasing of 2-3%. While the increase of % active site within 60-100 % provided % Ethanol conversion rising of

40%-80%. The ethanol molecules can be accessed the active site in eight-membered rings and ten membered rings more than the six-membered rings.

However, the optimum conditions from the simulation should be further confirmed the results with the laboratory in order to validate the simulation methodology. Further refinement of this simulation will be considered in our future correspondence.

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