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Modification of Natural Zeolite as a Catalyst for Steam Reforming of Toluene

Joko Waluyo [1]
Tobias Richards [2]
IGBN Makertihartha [1]
Herri Susanto [1]
[1] *Department of Chemical Engineering, Institut Teknologi Bandung, Jalan Ganesha 10 Bandung, Jawa Barat, Indonesia*
[2] *Swedish Center for Resource Recovery, University of Borås, SE-501 90 Borås, Sweden*
**e-mail:* herri@che.itb.ac.id

A catalyst for tar cracking has been prepared successfully from natural zeolites using ion exchange with NH_4NO_3, and acid leaching with HNO_3 solution for removing impurities and increasing pore volume. The activity of the modified zeolite was tested using toluene as a tar model compound. Tar conversion of about 54% was achieved in catalytic steam reforming at a temperature of 750°C using 2 gram of catalyst and the gas hourly space velocity about 5040 h^{-1}.

Keywords: ion exchange, acid leaching, tar catalytic cracking, mordenite, dealumination, gasification

INTRODUCTION

Depending on the biomass gasifier and the gasifying agent, biomass gasification may produce gaseous fuel for power generation or synthesis gas for chemical production. Unfortunately, gasification of biomass also produces tar as an undesired by product, which causes various problems in the downstream such as tar deposition on pipelines, filters, and valves, and catalyst deactivation of in the downstream processes (Anis and Zainal 2011).

Catalytic tar cracking offers some advantages over other methods, such as the conventional scrubbing water. Products catalytic tar cracking may increase the cold gas efficiency with increasing H_2 and CO content in the product gas. It is expected that catalytic tar cracking can be operated at a lower temperature than thermal cracking (Schmidt *et al.* 2011). Toluene is commonly used as a tar model in many research of the steam reforming of biomass-derived tar (Coll *et al.* 2001).

Recently, researches on catalyst development have been focused on the utilization of natural resources. Several mineral catalysts are being developed by various researchers: dolomite (Devi *et al.* 2005), olivine (Kuhn *et al.* 2008), ilmenite (Fredrik *et al.* 2013), limonite (Zou *et al.* 2016), calcite (Constantinou and Efstathiou 2009).

Zeolites are acidic material that can be utilized for cracking, hydrocracking and isomerization reaction. Some researchers use natural zeolite for cracking of n-hexane (Nasser *et al.* 2016) and hydrocracking of palm oil (Kadarwati *et al.* 2013). But natural zeolite requires a pre-treatment to remove impurities and to alter the pore structure and surface area. Dealumination and desilication may affect the transformation of pore structure, from microporous to the mesoporous structure. This is an important treatment since the microporous pore may hinder the mass diffusion promoting the formation of undesirable byproducts (Silaghi *et al.* 2014).

Experimental works reported in this paper dealt with the pre-treatment using ion exchange and acid leaching on natural zeolite from Wonosari, Yogyakarta. Catalyst activity test on the performance of toluene steam reforming is also reported here.

EXPERIMENTAL

Catalyst Preparation

Prior to modification, zeolite was pulverized into fine powder and then characterized by X-ray diffraction (XRD) and Energy Dispersive X-ray (EDX) to identify crystalline phase and to quantify the elemental composition.

Natural zeolite was initially washed with de-ionized water, dried and calcined at 550˚C for 12 hours to remove any impurities. Then, 1 gram of the sample was treated with the ion-exchange using 20 mL of 2M NH_4NO_3 at 90˚C for 2 hours. and then calcined again at the same conditions as before. This pretreated zeolite (called as catalyst Z-H) was then treated further with ammonium nitrate solution for exchanging Na^+ and K^+ cations with NH_4^+. Later NH_3 would evaporate during reheating the zeolite Z-H. The proton (H^+) bonded on the zeolite framework.

One gram of the ion-exchanged zeolite was treated further using 20 mL HNO_3 solution (1 M, 3 M, and 6 M) at 90˚C for 6 hours. Finally, the samples were washed, dried and calcined at 550˚C for 12 hours. Types of catalyst are presented in Table 1.

Catalyst Characterization

The XRD pattern was recorded over 2θ ranged from 5°-50° with speed of 76.8°/minutes and step size of 0.019. The SEM-EDX (Scanning Electron Microscopy-Energy Dispersive X-ray) and MP-AES (Microwave Plasma-Atomic Emission Spectroscopy) were used to identify and quantify the elemental component and Si/Al ratio. The pore properties were characterized BET method using Nova 3200e surface area and pore size analyzer.

Table 1. Natural zeolite treatment condition

No	Code	Ion exchange	Acid leaching
1.	Z-H	NH_4NO_3 2M, for 2 hours	-
2.	ZA-16	NH_4NO_3 2M, for 2 hours	HNO_3 1M, for 6 hours
3.	ZA-36	NH_4NO_3 2M, for 2 hours	HNO_3 3M, for 6 hours
4.	ZA-66	NH_4NO_3 2M, for 2 hours	HNO_3 6M, for 6 hours

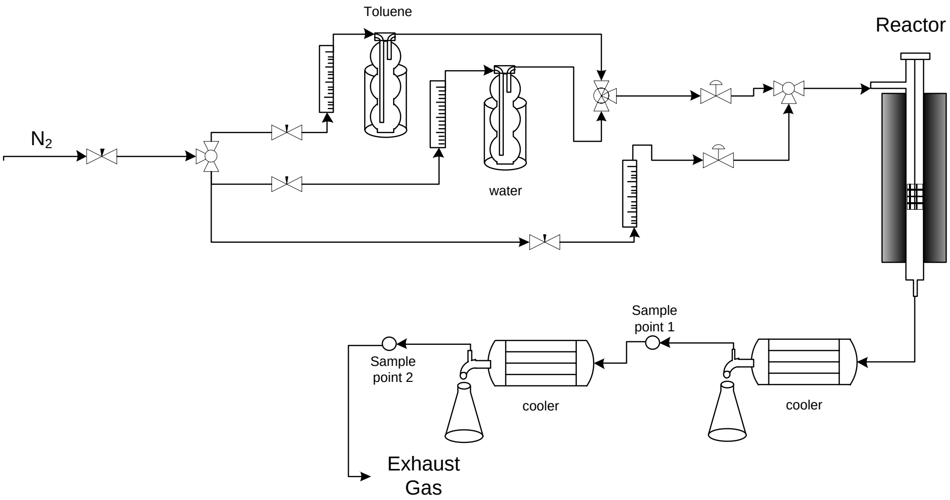

Fig. 1: Experimental Set up for Catalyst Activity Test

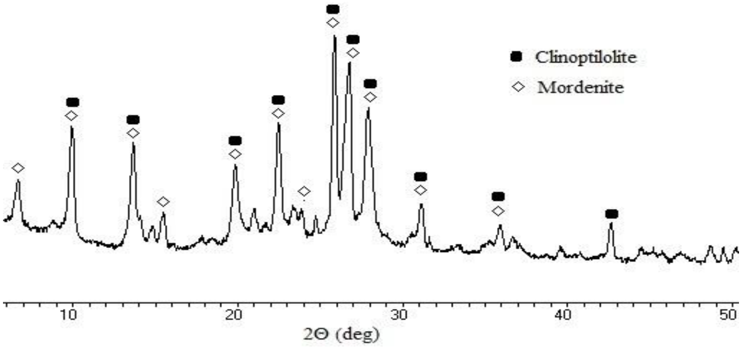

Fig. 2: XRD pattern of natural zeolite

The N_2 adsorption-desorption isotherm was recorded at a relative pressure (P/P_0) in the range of 0 to 0.99.

Activity Test of Catalyst

Two gram of catalyst obtained from the above-mentioned treatment were used in a packed bed catalytic reactor having an inner diameter of 1.5 cm and a length of 50 cm (**Fig. 1**). The operating conditions of the reactor were adjusted to 1 atm and 750˚C. The gas flow rate entering the packed bed reactor was adjusted at 1200 L/hour, with a concentration of toluene of 50 g/Nm^3. The steam to toluene ratio was adjusted of 10 g/g. Each experiment on toluene steam reforming was carried for 8 hours.

The concentrations of toluene at the inlet and the outlet of the reactor were analyzed using GC-FID (Shimadzu GC-14B). Determination of carbon deposit on the spent catalyst was carried out using TGA made in Rubotherm GmbH. In this experiment, the TGA temperature was set to rise with a heating rate of 10˚C/min, from 100 to 850˚C.

RESULTS AND DISCUSSION

Characterization of Catalyst

The XRD pattern showed that zeolite contained mordenite (MOR) and clinoptilolite (HEU) as dominant phases (**Fig. 2**). Some impurities were also detected as indicated by peaks.

Table 2. Zeolite composition as determined using EDX analysis

No	Element	Fresh Zeolite	after ion exchange (Z-H)	after acid leaching (ZA-66)
1.	C	0	2.55	5.68
2.	O	55.02	51.31	51.21
3.	Na	0.72	0.42	0.22
4.	Mg	0.87	0.53	0.53
5.	Al	7.09	7.85	7.23
6.	Si	30.47	32.47	31.48
7.	K	0.65	0.17	0
8.	Ca	3.06	2.15	1.72
9.	Ti	0.27	0.34	0.27
10.	Fe	2.57	2.21	1.65

Table 3. Physicochemical properties of modified zeolite

	Zeolite	Si/Al (%w)*	Pore diam.(Å)	A_{BET} (m^2/g)	V_{total} (cm^3/g)
1.	Z-H	5.09	38.1	16.0	0.094
2.	ZA-16	4.51	37.9	28.6	0.094
3.	ZA-36	4.91	38.2	50.7	0.107
4.	ZA-66	5.02	38.3	161.8	0.159

*analyzed using MP-AES

Elemental compositions of natural zeolite (results of EDX analysis) are presented in **Table 2**. The result shows that in addition to cation Na^+ and K^+, natural zeolite also had cation Ca^{2+} and Mg^{2+} in the zeolite framework. Natural zeolite also contained free oxides such as Al_2O_3, SiO_2, CaO, MgO, Na_2O and K_2O which may cover the zeolite pores or active sites leading to decreased activity. Several of these metals had a relatively low melting point, so it may cause problems during tar cracking at elevated temperature. Hence it is necessary for natural zeolite to be modified by thermal and chemical treatments such as ion exchange and acid leaching.

Effect of Zeolite Modification

The cation content of natural zeolite (Na, K, Ca and Mg) decreased after ion exchange and calcination (Table 2). Even though modification by ion exchange has been successfully done, the zeolite surface area and pore volume were still quite low (**Table 3**). Therefore there is a need for further modification by acid leaching using HNO_3. Acid leaching can remove impurities, causes dealumination and might establish extra-framework aluminum (EFAL) (Zanjanchi and Hemmati 2004).

The XRD results presented in **Fig. 3** shows that the crystallinity of the zeolite mordenite phase did not change significantly by ion exchange and acid

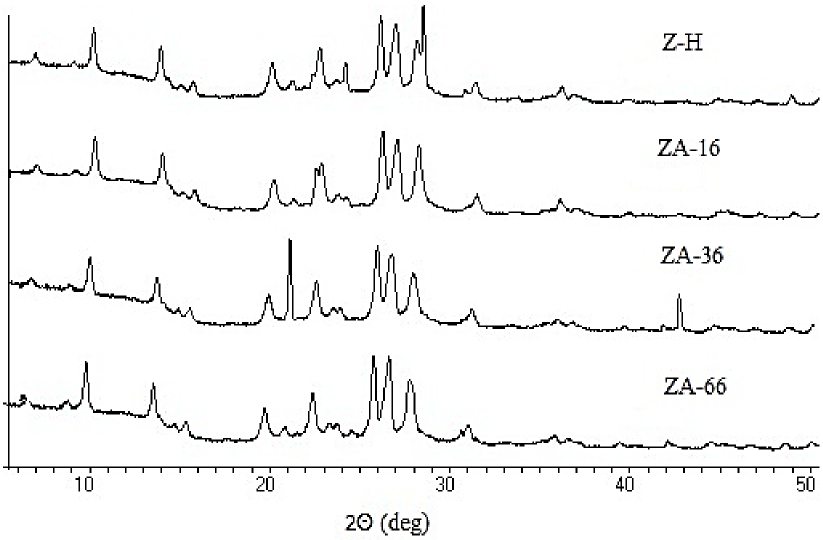

Fig. 3: XRD pattern after modification

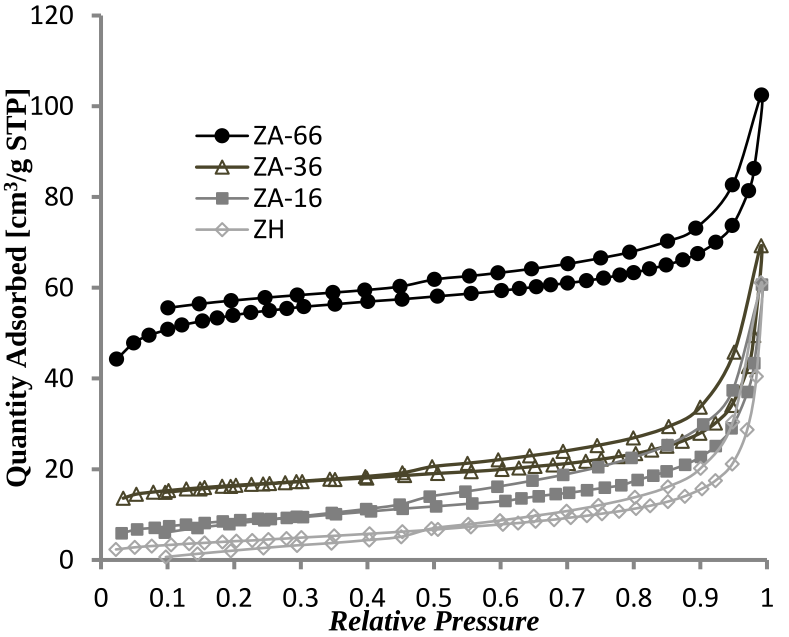

Fig. 4: N_2 adsorption/desorption isotherms of modified natural zeolite

leaching treatment at various concentrations. The disappearance of part of the diffractogram from XRD analysis results indicates partial loss of impurities from the modified zeolite.

N_2 adsorption-desorption isotherm showed forms of the hysteresis loop in the P/P_0 range of 0.5-0.99 (**Fig. 4**). This isotherm is classified as type IV in IUPAC classification. The appearance of hysteresis loops indicates the formation of mesopores by the acid leaching. The acid leaching of natural zeolite removed some impurities and aluminum atoms from zeolite framework, leading to a partial change in the pore structure and increase in pore volume while maintaining the pore diameter approximately 38Å.

The removal of Al atoms by breaking Al-O bond on the zeolite framework by acid leaching would form the extra-framework aluminum (EFAL). This was indicated by Si/Al ratio which is not significantly changed, while the zeolite surface area increased significantly **(Table 3**). The same results as the study by Zanjanchi and Hemmati (2004) prove that the extra-framework aluminum (EFAL) was formed on zeolite L by acid leaching using hydrochloric acid. EFAL was also formed during ion exchange and calcination process. The amount and distribution of extra-framework aluminum are associated with catalytic activity and selectivity of the zeolite. Increasing the HNO_3 concentration resulted in the decrease of impurities as well as an increase in the amount of EFAL formed on the zeolite, as indicated by the increasing pore volume and surface area of the zeolite.

Catalytic Activity Test

The catalytic activity of modified zeolite as steam reforming catalyst was tested by applying the modified zeolite in a fixed bed reactor for the catalytic cracking of tar with toluene as tar model compound. Steam reforming of toluene and cracking reaction may be represented by equation (1)-(3).

$$C_7H_8 + 7H_2O \rightarrow 7CO + 11H_2 \qquad (1)$$

$$C_7H_8 \rightarrow C^* + C_xH_y + \text{gas} \qquad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (3)$$

The concentration of toluene used in steam reforming was 50 g/Nm^3, which correspond to tar content in product gas from an updraft gasifier. An excessive amount of steam (stoichiometric) was used to reduce the potency formation of carbon deposit. Toluene conversion and carbon deposits formation over modified zeolite as a catalyst were shown in **Fig. 5**.

In accordance with the study by Heo *et al.* (2016) on the effect of K and Ca

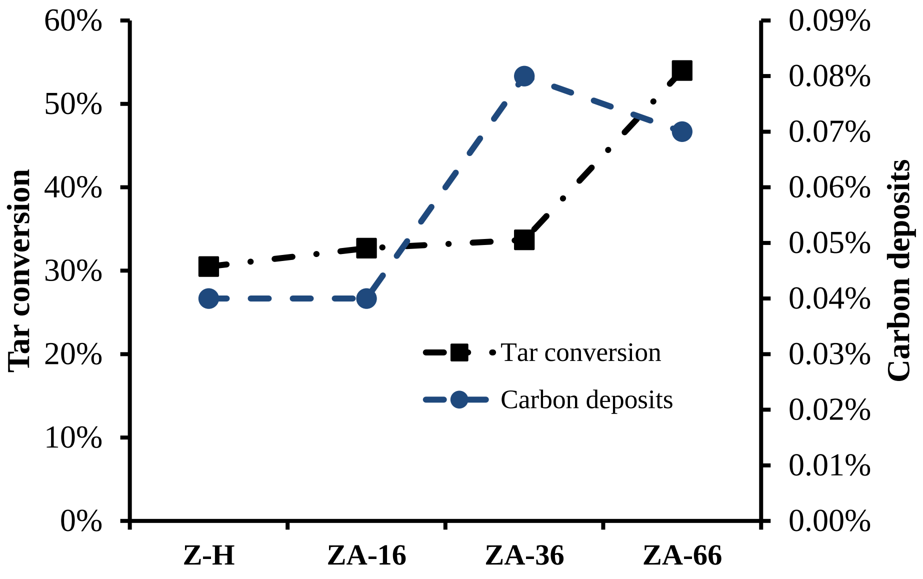

Fig. 5: Tar conversion and carbon deposits with S/T 10, initial toluene 50 g/Nm^3

addition on steam reforming catalyst, the presence K and Ca did not increase the catalyst activity. Therefore the existence of Na, K and Ca cation can be considered as impurities in the catalyst. Pore volume and surface area can be increased by removing the mentioned impurities. Increasing the surface area of catalyst would enhance contact between toluene and steam, which leads to steam reforming reaction. In agreement with the results from the activity test, ZA-66 which has the greatest surface area results in increased conversion.

Dealumination process of zeolite by acid leaching to increase the ratio of Si/Al, improved the thermal strength of the zeolite, so when in contact with steam of high temperature, the zeolite pore would not easily collapse. Dealumination process usually reduced the acid site of the zeolite. In this study, acid leaching by HNO_3 at different concentrations did not change the Si/Al ratio significantly as shown in **Table 3**, hence zeolite acidity remains relatively stable. Based on research by Zanjanchi and Hemmati (2004), using acid leaching at high concentrations indicate that the formation of extra-framework aluminum (EFAL) can improve the acid site to a certain extent. Zeolite catalyst is more active due to higher acidity and therefore the amount of acid site for catalytic cracking (Buchireddy *et al*. 2010). Hence, low Si/Al ratio results in zeolite of higher acidity making it more suitable for use as catalyst for catalytic cracking or steam reforming.

Thermogravimetric analysis results in a slight formation of carbon deposit (less than 1%) on the catalyst after activity test. Steam reforming conducted at 750˚C gave positive results in which the conversion increases with a decrease in carbon deposit formation due to water gas reaction and Boudouard reaction, as shown in reaction (4) and reaction (5).

$$C^* + H_2O \rightarrow CO + H_2 \qquad (4)$$

$$C^* + CO_2 \rightarrow CO \qquad (5)$$

Thermodynamically, the reaction of carbon with water that produces CO and H_2 is favorable at high temperature (more than 700˚C), while the reaction of carbon with CO_2 is favorable at the temperature above 830˚C (Simell *et al*. 1997). The presence of Fe and Mg in natural zeolite may reduce carbon deposit formation that may deactivate the catalyst and thus Fe and Mg are frequently used as a promoter in the catalyst to prevent coke deposition (Laosiripojana *et al*. 2014, Yue *et al*. 2010).

CONCLUSIONS

Acid leaching at various concentration of HNO_3 did not significantly alter the Si/Al ratio and the crystallinity of the zeolite mordenite phase. Zeolite modification by ion exchange and acid leaching were able to remove impurities such as Na, K, Ca and increase both the pore volume and the surface area of zeolite while also increasing the presence of mesopores.

Zeolite ZA-66 had the better activity to toward toluene conversion as compared to ZH, ZA-16, and ZA-36. The higher activity by acid leaching with 6M HNO_3 solution was attributed to its surface area and relatively higher acidity.

The excessive amount of steam used was sufficient to reduce the formation of carbon deposits. The presence of Mg and Fe is advantageous in the natural zeolite to be used as a catalyst which prevents the formation of carbon deposit. The presences of nickel on modified zeolite have a potential to increase the catalyst activity and thus toluene conversion.

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