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Synthesis Dimethyl Ether from Methanol Using Red Mud Catalyst

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Abstract. Dimethyl ether (DME) is apromising alternative for substituting petroleum fuel including gasoline, liquified petroleum gas, and diesel. In this research, the utilization of red mud as catalyst was investigated to dehydrate methanol to Dimethyl Ether (DME). Red mud is a solid waste from the bauxite industry which lead to environmental issues if did not treat properly. The catalyst characteristics were determined in terms of porosity, crystallinity, elemental composition, and pores size distribution. The catalysts activity was evaluated in a fixed-bed reactor at temperature range 200-300 °C. The influence of different parameters, including temperature and type of catalyst were varied to obtain the optimum reaction condition. The results revealed that the highest methanol conversion was 68% at temperature of 300 °C when using calcined red mud catalyst.

Introduction

Currently, crude oil is the main energy source in Indonesia, however, the proven oil reserves are diminishing. Consequently, the increase in crude oil consumption has caused Indonesia an oil importer. One of the efforts to diversify energy is by substituting diesel fuel with dimethyl ether (DME). The use of dimethyl ether as a vehicle fuel has several advantages, including: the combustion result of dimethyl ether has a low NOx gas content so it is more environmentally friendly, low engine noise (indicated by combustion performance and high cethane numbers) and produce low smoke points [1]. Another advantage of dimethyl ether is that this compound is renewable because it can be made from synthesis gas which can be generated from biomass.

Dimethyl ether is the simplest ether compound. The characteristics of DME are a colorless, noncorrosive, noncarcinogenic nontoxic, and environmentally friendly [2]. It is stored as liquid in pressurized tanks due to has a boiling point of −25 °C. Moreover, DME has a high cetane number compared to the conventional diesel [3]. It can be generated from dehydration of Methanol using a solid acid bimolecular catalyst. Methanol which as raw material can be produced from synthesis gas derived from natural gas, coal gasification or the results of the biomass process [4]. The Bronsted and Lewis acid were as active sites on the surface to catalyze reaction. Nevertheless, when the strength of acid sites is too high, it could promote further DME dehydration to form olefins and hydrocarbons.

Various catalysts include zeolites [4-9], γ-alumina [10-13], Heteropoly acid [14, 15], clay [16, 17], diatomite [18], mesoporous silica [5] and silica alumina exhibited DME selectivity and high methanol conversion at high temperatures and pressures. Many researchers have also studied the application of metal oxide supported on modified materials [19-21] for the methanol dehydration to DME. Meanwhile, ion exchange resin catalyst can be applied at lower temperatures, and contrary it cannot be used at high temperatures [22]. At low temperature, the dehydration methanol will avoid side reactions, such olefins, or hydrocarbons formation. The coke deposit also can be hindered. Several factors, including acidity, pore size diameter, pore size distribution, and thermal stability are the important considerations in the choice of catalyst in DME synthesis.

Red mud is a solid residue that resulted from the bauxite processing to produce aluminum oxide. In Indonesia, every year around 1 million tons of red mud was generated and potentially causes environmental problems. The main compositions of red mud are several metal oxides including Fe_2O_3, SiO_2, Al_2O_3, and TiO_2. The metal oxides are necessary to catalyze methanol dehydration to form DME. Red mud is a potential candidate to obtain sustainable and cheap material as a catalyst,

as well as to purpose the waste handling. The purpose of the study is to investigate the red mud application as catalyst on its activity in the methanol dehydration to DME. The catalyst activity is tested at various reaction temperatures in a fixed-bed reactor under atmospheric pressure. In addition, XRD, N2 adsorption-desorption, and XRF analysis were employed to determine the characteristics of red mud catalysts.

Experimental Method

Materials and Catalyst Preparation. Methanol p.a. was purchased from Merck. Red mud was collected from bauxite mining industry in West Kalimantan, province, Indonesia. Prior to use, red mud was dried and then crushed using a mill. The resulting powder were sieved to gain uniform particles size of 0.5–1.0 mm. Red mud composition was calculated using X-ray fluorescence (XRF). Preparation of catalysts techniques have been conducted by simple calcination as described elsewhere. The raw red mud was calcined at 800 °C for 4 h using a heating rate of 5 °C/minute.

Catalyst Characterization. The porosity of catalysts was determined by N_2 physisorption. The cristanillity was anayzed using X-ray diffraction (XRD) to determine the phases.

Catalyst Testing. A fixed-bed reactor was applied to carry out experiments at atmospheric pressure. Prior to the dehydration, the N_2 was flown through the reactor to activate and maintained at the preferred temperature. The methanol dehydration reaction was studied with a Weight hourly space velocity (WHSV) of 1.1 $g^{-1}.h^{-2}$ and N_2 was employed as a sweeping gas. A gas chromatograph with FID was applied to analyze the products.

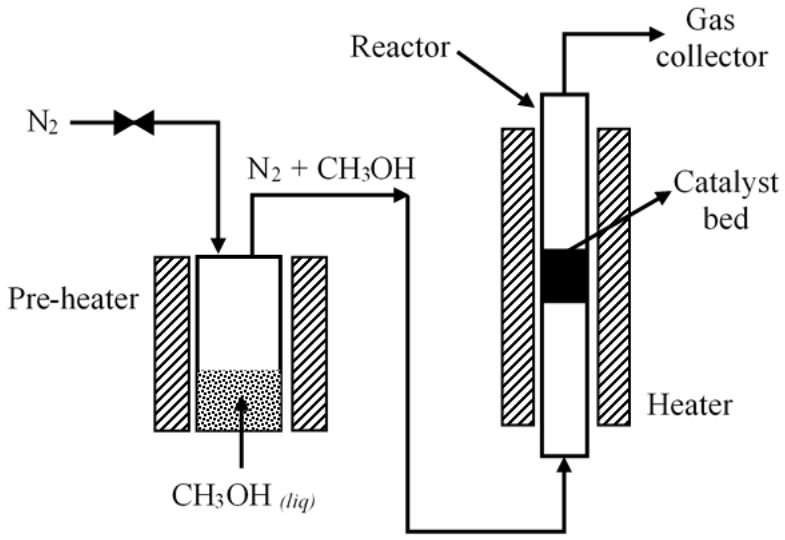

Fig. 1. A fixed-bed reactor for Dehydration Methanol to DME using Red Mud Catalyst.

Results and Discussion

Catalyst Characterization. The specific surface area of calcined red mud (82.2 $m^2.g^{-1}$) was larger than the raw red mud (27.14 $m^2.g^{-1}$). The calcination process affected the porosity of catalyst, which resulted in the increase in the specific surface area, increase in pore volume, and decrease in the average pore size. The pore size distribution of calcined red mud shows an increase in particle size due to the reduction of impurities which could provide an increase of specific surface area and pore volume. Fig. 2 are presented the pore size distributions of the raw and calcined red mud. According to Table 1, the chemical composition of red mud in raw and calcined red mud was mainly Al_2O_3 and Fe_2O_3.

Table 1. The Chemical Composition of Red Mud.

Sample	Al_2O_3	SiO_2	CaO	TiO_2	Fe_2O_3	NiO	Others
Raw Red Mud	47.69	19.53	1.83	0.29	29.26	0.02	1.38
Calcined Red Mud	49.14	20.16	1.41	1.12	27.93	0.01	0.23

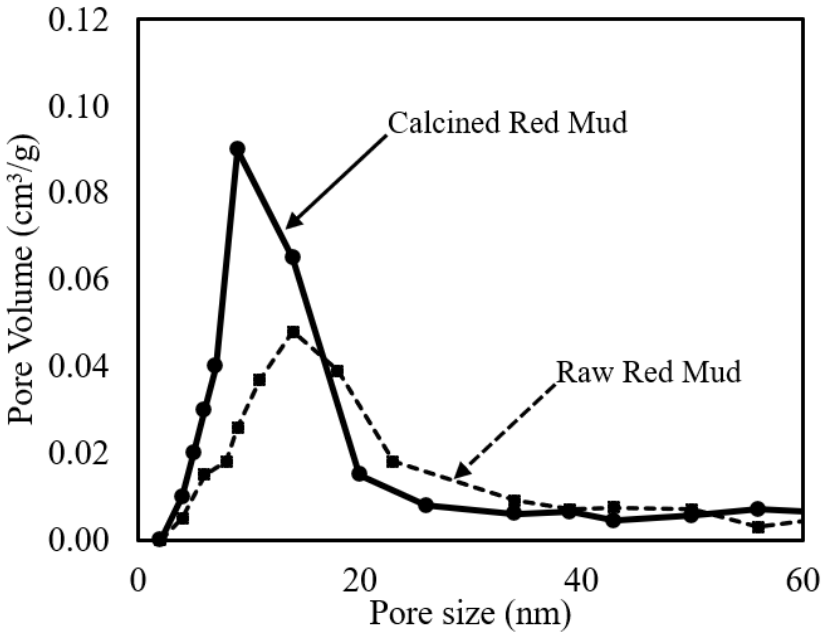

Fig 2. The Pore Size Distributions of the Raw and Calcined Red Mud.

Furthermore, the crystal structure analysas using XRD showed that the raw and calcined red mud catalysts have no significant changes occurred after the catalyst preparation as presented in Fig. 3. After calcination, the calcined red mud some peaks were disappeared which was attributed to the loss of some hydrate components. The major phase after calcination in the structure was hematite and Al_2O_3.

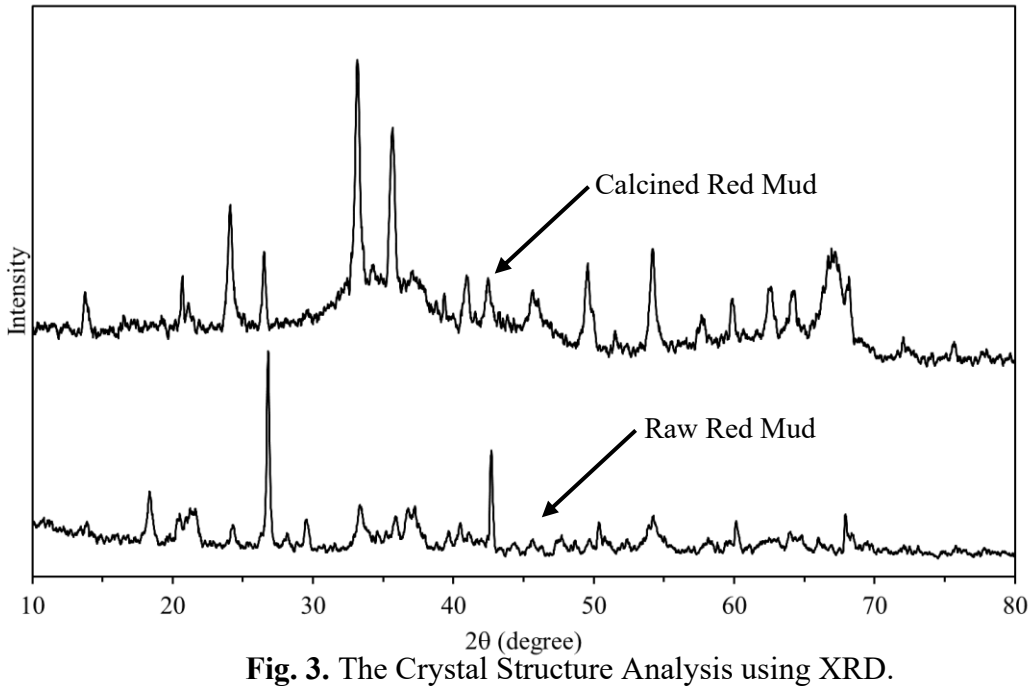

Fig. 3. The Crystal Structure Analysis using XRD.

Catalyst Testing

Fig. 4 presents the influence of temperature on methanol conversion in the dehydration reaction using calcined and raw red mud catalyst. Both the calcined and raw red mud catalyst show a similar trend, that is the higher the temperature will result in conversion. When the temperature increased from 200 to 250 °C, the conversion of methanol increased from 57% to 64% for calcined red mud catalyst. The maximum methanol conversion was obtained at 68% and achieved at 300 °C. Meanwhile, when using raw red mud catalyst catalyst, methanol conversion also increased from 52 to 63% at an increase in temperature from 200 to 300 °C. It can be concluded that the raw red mud catalyst performs less active than calcined red mud catalyst. It could be due to the increase in the acidity of the catalyst due to the calcination process of the raw red mud. The presence of a strong acid site not only facilitates the dehydration reaction but also encourages the formation of hydrocarbons. Red mud preparation by calcination seems to give significant results to increase methanol conversion.

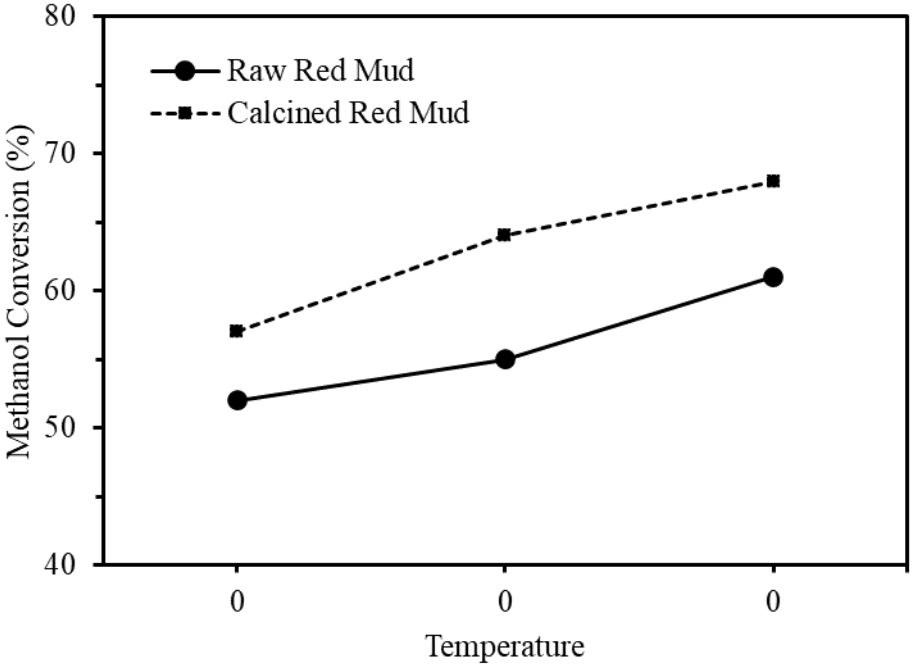

Fig 4. The Influence of Temperature on Methanol Conversion in the Dehydration Reaction.

Fig. 5 shows the selectivity of DME when applying calcined and raw red mud catalyst during the methanol dehydration reaction. When the reaction temperature increases, the DME selectivity decreases in both the calcined and raw red mud catalyst as shown in Fig. 6. DME selectivity in the methanol dehydration reaction using the calcined red mud catalyst decreased from 60.3 wt% to 54.3% when the reaction temperature increased from 200 to 300 °C. The same results were obtained when using a raw red mud catalyst, where the selectivity decreased from 61% to 50% when the reaction temperature was increased. The DME selectivity obtained in the methanol dehydration reaction with calcined red mud catalyst showed a higher percentage compared to the raw red mud catalyst. Selectivity to DME starts to decline at temperatures above 200 °C, forming short chain aliphatic hydrocarbons (C1 to C3) resulting from cracking of methanol so that it will decrease the selectivity of DME. It is possible that at high temperatures accompanied by deactivation of the catalyst due to the formation of coke. At high temperatures CH_4 and CO will be produced as the main byproducts due to the decomposition of methanol and DME.

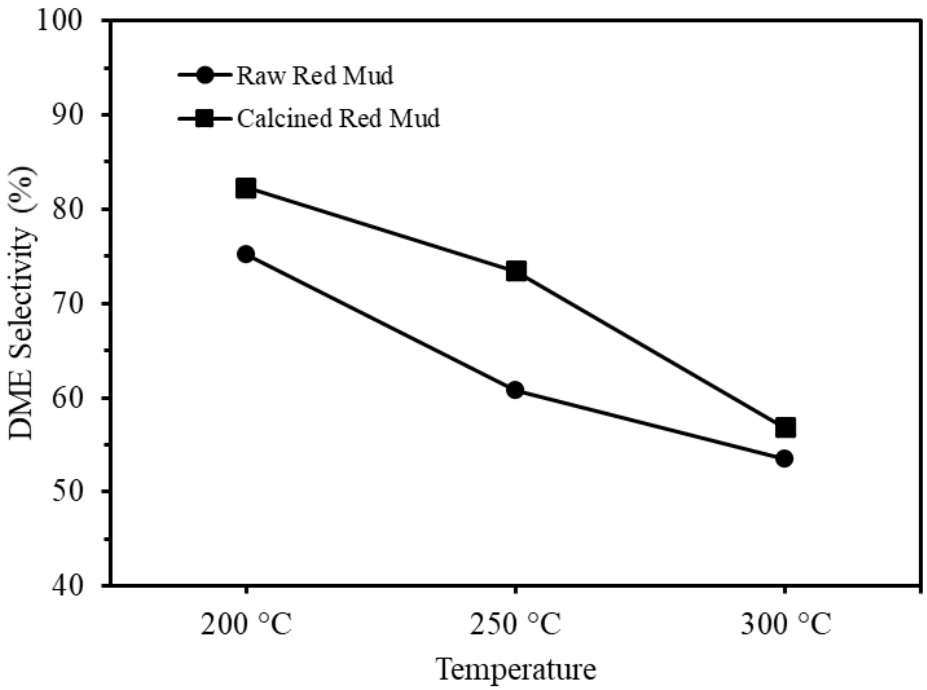

Fig 5. The Influence of Temperature on DME Selectivity in the Dehydration Reaction.

Conslucions

In this study, the influence of catalyst on the dehydration of methanol to DME was investigated. It can be concluded that the calcined red mud catalyst exhibited more active compare to raw red mud catalyst in terms of Methanol conversion. The high methanol conversion (68%) was achieved at the temperature of 300 °C. However, the DME selectivity reduced as temperature elevated from 200 to 300 °C.

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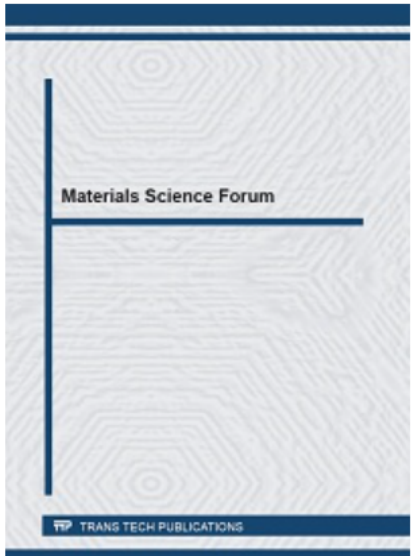

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