

Dehydration Isopropyl Alcohol to Diisopropyl Ether over Molybdenum Phosphide Pillared Bentonite

Hasanudin Hasanudin^{1,2*}, Wan Ryan Asri¹, Kristina Tampubolon¹, Fahma Riyanti¹, Widia Purwaningrum¹ and Karna Wijaya³

¹Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Sriwijaya, Inderalaya 30662, South Sumatra, Indonesia

²Biofuel Research Group, Faculty of Mathematics and Natural Science, Universitas Sriwijaya, Inderalaya 30662, South Sumatra, Indonesia

³Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia

ABSTRACT

Emissions from gasoline are one of the contributors to air pollution. Diisopropyl ether (DIPE) is an alternative oxygenate additive that can improve gasoline quality, minimizing CO and hydrocarbon gas emissions during combustion. However, there are very few studies on the use of pillared bentonite-based catalysts for DIPE production. This study aims to produce DIPE via dehydration of isopropyl alcohol using a molybdenum phosphide pillared bentonite (MoP-Bentonite) catalyst. The effect of Mo⁶⁺ metal concentration on the catalytic activity of isopropyl alcohol dehydration was also investigated. The catalyst that gives the highest DIPE yield will be analyzed by X-ray Diffraction (XRD), Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX), Gas Sorption Analyzer (GSA), and total acidity using the gravimetric method. In addition, the dehydration product will be

analyzed by Gas Chromatography-Mass Spectroscopy (GC-MS). The results showed that MoP has been successfully pillared into bentonite and showed an increase in surface area, acidity, and catalytic activity. The highest yield of DIPE was obtained using a 4 mEq/g MoP-Bentonite catalyst with a DIPE yield of 64.5%.

Keywords: Alcohol dehydration, bentonite, molybdenum phosphide, pillared bentonite

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E-mail addresses:

hasanudin@mipa.unsri.ac.id (Hasanudin Hasanudin)

wanryanryan@gmail.com (Wan Ryan Asri)

tampubolonkristina4@gmail.com (Kristina Tampubolon)

fatechafj@yahoo.com (Fahma Riyanti)

purwaningrum@unsri.ac.id (Widia Purwaningrum)

karnawijaya@ugm.ac.id (Karna Wijaya)

*Corresponding author

INTRODUCTION

Air quality is very influential on the health of living things. Unfortunately, 92% of the world's population, such as Asia, Africa, and the Middle East, are excessively exposed to high air pollution concentrations, and the average is beyond the limits set by the World Health Organization for pollutants (Li et al., 2020). Air pollution causes several chronic diseases and human respiratory tract infections. One of the contributors to air pollution in greenhouse gases (GHG) is the burning and consumption of fossil fuels such as gasoline. Therefore, it is essential to formulate alternative fuels that emit fewer pollutants and could completely combustion (Al-Arkawazi, 2019; Kashyap et al., 2020). Complete combustion is one possible way to increase the efficiency of petroleum fuels such as gasoline (Zhu et al., 2011).

Gasoline oxygenate additives such as methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE) are generally used to increase the octane number and oxygen content, which positively correlated with gasoline quality. However, MTBE poses problems due to its toxicity and groundwater contamination (Fan et al., 2021). ETBE, on the other hand, is productive in the market, but relatively insufficient supply is becoming a problem (Ahmadi & Almasi, 2020). Diisopropyl ether (DIPE) is a gasoline additive that can overcome these shortcomings because of its environmentally friendly nature, increasing octane number, improving combustion conditions that reduce CO emissions, and better compatibility (Uyumaz et al., 2020; Wang et al., 2020). Furthermore, DIPE production can generally be obtained through the dehydration of isopropyl alcohol (Muñoz-Rujas et al., 2017), and a catalyst can be used to increase the reaction rate.

Solid catalysts such as zeolites and γ -alumina have produced ether compounds via dehydration alcohol. However, γ -alumina exhibits lower dehydration catalysis activity which is possible due to the formation of water molecules at the Lewis acid site (Said et al., 2014). Combinations of these catalysts with transition metals have also been reported (Hasanudin et al., 2020). Furthermore, Armenta et al. (2019), using Fe_3O_4 , CuO, and Fe_3O_4 -CuO, impregnated alumina catalysts, and it was reported that $\text{Fe}_3\text{O}_4/\gamma$ -alumina gives conversion with the highest DIPE selectivity of 55%. Therefore, it is vital to develop new catalysts to increase DIPE yield through dehydration of isopropyl alcohol.

Bentonite is a potential catalyst to produce DIPE via alcohol dehydration because of its specific properties and structure, large abundance, and low cost. Bentonite, a type of clay with a smectite mineral content of 85–95%, is plastic with high colloidal properties, high ion-exchange capacity ability, and absorbs large amounts of cations between layers (Belousov et al., 2019). The weakness of bentonites, such as low surface area, acidity, and lack of permanent porosity, can be improved by structure modification through pillarization. Pillarization is a metal distribution process in bentonite through intercalation of a pillar agent metal hydroxy cations into the silica layers in the clay structure (Aziz et al., 2019).

This process increases the basal spacing, pore volume, surface area, and thermal stability, which are great for catalytic purposes.

Transitional metals such as Al, Zr, Ti, Cr, and others have been used as pillars individually or in a mixture. The transitional group elements show greater benefit than the main group elements (Rinaldi & Kristiani, 2017). Modification of transition metals using sulfides, phosphides, and others are on developing (Carenco et al., 2013). Among the modifications that have been made, metal phosphide has advantages in terms of catalytic efficiency, abundance, stability, and being environmentally friendly (Ruddy et al., 2014; Wu et al., 2019). Among metal phosphide studies, MoP is more active than other metal modifications and has been used in various catalytic reactions and good cycle resistance (Alvarez-Galvan et al., 2019; Cheng et al., 2007) and reported having a high surface area and a dominant active site (Deng et al., 2015). The metal and P sites serve as proton acceptors, and the hydride receptor center is located on the catalyst surface (Sun et al., 2020). Mo⁶⁺ on MoP has been reported to contribute as an active site in the catalytic reaction of furfural alcohol dehydration (Chan et al., 2019).

Studies on the production of DIPE by dehydration of isopropyl alcohol using a molybdenum phosphide pillared bentonite catalyst have not been reported. Pillarization is expected to improve the catalytic and material properties of the catalyst. Considering that the concentration of pillar metal affects the catalyst properties (Mnasri et al., 2017), thus the study of the effect of Mo⁶⁺ concentration on the catalytic activity of dehydration will be investigated. The catalyst that gives the highest DIPE yield will be analyzed by X-ray Powder Diffraction (XRD), Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX), Gas Sorption Analyzer (GSA), and compared with Na-Bentonite as a control. In addition, the dehydration product will be analyzed by Gas chromatography-mass spectroscopy (GC-MS).

MATERIALS AND METHODS

Na-Bentonite Preparation

Natural Bentonite (Bayan, Central Java) that is already in the form of powder was sieved using a 200-mesh sieve. In order to increase the sodium content, saturation was done by adding 250 g bentonite to 1000 mL of a saturated sodium chloride solution. After that, the solution was stirred for about 48 hours with a magnetic stirrer. The solution was then washed with distilled water and with the help of centrifugation to speed up the process and wash away contaminants in the solution. The centrifugation process was repeated four times with a speed of 6000 rpm. A test was carried out using 0.1 M AgNO₃. AgNO₃ was dripped to the solution to ensure the washing was successful. If there is no white precipitate in the solution, bentonite is considered clean of chloride ions. The clean bentonite surface was dried in the oven at 80°C until it could be crushed easily with mortar. The powder of

Na-Bentonite was sieved once more with a 200 mesh sieve and was analyzed using XRD, SEM-EDX, and BET.

Na-Bentonite Cation Exchange Capacity (CEC) Determination

The determination of CEC was first done by making the complex solution of $[\text{Cu}(\text{en})_2]^{2+}$. 3.98 g of CuSO_4 was added to 250 mL of distilled water to make a 0.1 M CuSO_4 solution. 3.38 mL of ethylenediamine 99% was diluted with 100 mL distilled water to make 0.5 M ethylenediamine solution. The λ_{max} of the solution is then determined by using a UV-Vis spectrophotometer (Shimadzu). An amount of 0.1 g of natural bentonite and Na-Bentonite was added to 25 mL of 0.01 M $[\text{Cu}(\text{en})_2]^{2+}$. The solution was stirred using a magnetic stirrer for 30 minutes then filtered using filter paper. The absorbance of the supernatant was measured at a wavelength of 547 nm using a UV-Visible spectrophotometer. The concentration of standard solution $[\text{Cu}(\text{en})_2]^{2+}$, such as 6×10^{-3} , 7×10^{-3} , 8×10^{-3} , 9×10^{-3} , and 10×10^{-3} M was used to create a calibration curve.

Synthesis of Molybdenum Phosphide Pillared Bentonite with Mo^{6+} Concentration Variation

According to Shao et al. (2013), an amount of 5 grams of Na-Bentonite was added to 66.65 mL of molybdenum heptamolybdate solution for a concentration of 2 mEq/g then stirred for 1 hour. These steps were repeated using variations in the amount of metal in Na-Bentonite with a ratio of 133.3 mL, 200 mL, 266,7 mL, and 333.3 mL for 4, 6, 8, and 10 mEq/g, respectively. According to Deng et al. (2015), when stirring takes place, the solution is dripped with a 0.5 M $(\text{NH}_4)_2\text{HPO}_4$ solution at a 1 mL/minute rate with the volume of molar ratio $\text{Mo}:\text{P} = 1:3$. Next, an amount of 10 mL of 0.5 M $(\text{NH}_4)_2\text{HPO}_4$ solution is dripped for a concentration of 2 mEq/g and stirred using a magnetic stirrer for 24 hours. These steps were repeated using variations in the volume of molar ratio in the amount of 20 mL, 30 mL, 40 mL, and 50 mL 0.5 M $(\text{NH}_4)_2\text{HPO}_4$ solution for 4, 6, 8, and 10 mEq/g, respectively. After that, the mixture was heated for 24 hours at 80°C using an oven to remove the moisture content. Next, the solids were crushed, sieved with a 200 mesh, and calcined at 350°C for 30 minutes.

MoPO_4 -Bentonite Reduction into MoP-Bentonite

An amount of 5 grams of MoPO_4 pillared bentonite were added to 50 mL distilled water and stirred using an ultrasonic cleaner for 5 minutes. After that, an amount of 0.629 grams of NaBH_4 were added and stirred using an ultrasonic cleaner for 30 minutes. The reduction process is considered done if bubbles are formed. The mixture was filtered using a vacuum pump, and the precipitate was taken then heated at 80°C using an oven. The dried solids

were crushed then sieved with a 200 mesh sieve, and the powder was called MoP-Bentonite (Totong et al., 2020).

Isopropyl Alcohol Dehydration

According to Hosseini et al. (2012), the reflux apparatus is prepared using a neck flask, condenser, water bath, and thermometer. First, an amount of 50 mL of isopropyl alcohol was put into the neck flask. Then, an amount of 0.5 grams of MoP-Bentonite was added. Next, the neck flask was put into a container filled with oil then refluxed for 3.5 hours at 160°C. The product of isopropyl alcohol dehydration was characterized using GC-MS (Thermo Scientific) with an operation set as such; helium as the carrier gas, the rate of flowed gas at 30mL/min, column temperature of 200-230°C, and detector temperature of 350°C. Then, the procedure was repeated with five different mEq of MoP-Bentonite catalysts. The catalyst with the best activity was characterized using XRD, SEM-EDX, GSA, and acidity analysis.

Catalyst Characterization

Crystallinity and mineral content analysis was measured using X-Ray Diffraction (XRD) (Rigaku Minu Flex 600). The operation condition of XRD were X-ray tube: Cu (1.54060 Å), voltage: 40.0 kV, current: 30.0 mA, step size: 0.0200 deg, and count time: 0.24 seconds. The results of X-ray diffraction measurements were diffractograms. Based on the diffractogram, the structure and quality of the crystals can be known. Analysis of catalyst surface area, total pore volume, and pore radius was performed using the Gas Sorption Analyzer NOVA 1000 based on the Brunauer-Emmet-Teller (BET) method. The pore surface and elemental content of the catalyst were analyzed using Scanning Electron Microscopy (SEM) with EDX detector (JSM 6510). Analysis of acidity of catalyst was taken using gravimetric method. An amount of 0.5 grams of MoP-Bentonite catalyst was put into a crucible with a known weight then the crucible with catalyst was weighed once more. The crucible containing MoP-Bentonite was put into a desiccator equipped with a tap and a hole in the lid, then the desiccator was vacuumed for 60 minutes and then flowed with 5 mL of ammonia gas for 24 hours. After 24 hours, the catalyst was weighed, and the ammonia absorbed by the MoP-Bentonite catalyst was calculated using the gravimetric method (Mara et al., 2016).

RESULTS AND DISCUSSIONS

Preparation and Determination of Bentonite and Na-Bentonite CEC Value

Bentonite was saturated using NaCl to substitute the cations in the bentonite interlayer into Na⁺, thus making the cations uniform. This condition will increase the distance

between the bentonite layer; therefore, the pillarization will occur more easily. The Na⁺ ion exchange in the bentonite layer has been reported could increase the swelling properties of bentonite (Hayakawa et al., 2019). Furthermore, the Na⁺ cation was chosen because it has a monovalent valence number that can increase swelling more significantly than the divalent valence cation (Ahmed et al., 2016).

Determination of bentonite and Na-Bentonite CEC value was done using the calibration curve method. The initial, final, and adsorbed concentration of [Cu(en)₂]²⁺ complex in mmol/mL showed in Table 1.

The CEC value obtained from natural bentonite was 165.85 mEq/100g, and Na-Bentonite was 279.15 mEq/100 g. The increase of CEC indicates that Na⁺ cations would be easily exchanged through pillarization by Mo⁶⁺ metal (Mnasri-Ghnimi & Frini-Srasra, 2014). This trend was consistent with a previous report (Kırpçak & Kalpazan, 2020). The greater the CEC value, the more Mo⁶⁺ metal could replace the Na⁺ cations. On the other hand, if the CEC value of Na-Bentonite was smaller than bentonite, it indicates that the cationic exchange would occur irreversibly and was difficult to exchange with other ions (Mnasri et al., 2017).

Table 1
The CEC value of Bentonite and Na-Bentonite

Sample	Initial concentration	Final concentration	Absorbed concentration	CEC value (mEq/100 gram bentonite)
Bentonite	0.01	0.006683	0.003317	165.85
Na-Bentonite	0.01	0.004413	0.005583	279.15

Catalyst Characterization

XRD analysis was carried out to see the diffraction pattern at 2θ and the distance between the planes. The shift between of two angles can indicate the success of the pillarization. Figure 1 shows the diffractogram of Na-Bentonite and MoP-Bentonite 4 mEq/g catalyst. MoP-bentonite of 4 mEq/g concentration was chosen because the catalyst provided the best catalytic activity according to its highest DIPE yield compared to other catalysts' concentrations.

X-ray diffractogram of Na-Bentonite shows the characteristics of bentonite peaks at 2θ values around in 6.02°, 26.00°, 28.04°, and 40.43° (JCPDS No: 29-1499), similarly found have been reported by a previous study (Akkouche et al., 2020), while MoP-Bentonite shows the characteristic of bentonite peaks at 2θ values around in 7.22°, 26.30° and 28.30°

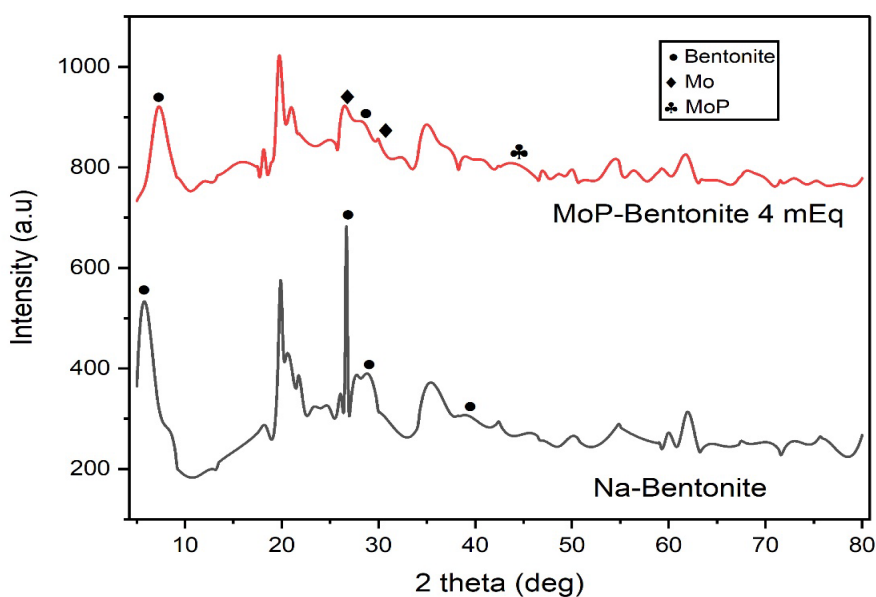


Figure 1. X-ray diffractogram of Na-Bentonite and MoP-Bentonite catalyst

(JCPDS No. 26-1449). From the results of the XRD analysis, it can be concluded that Na-Bentonite has a characteristic of 2θ at 6.02° , and after the pillarization, there is a shift to 7.22° . The 2θ changes from a smaller to a larger indicates the presence of another cation Mo on the bentonite surface (Zaghouane-Boudiaf et al., 2014). Similar results have been reported by Kıpçak and Kalpazan (2020) in other modified bentonites. Furthermore, the 2θ peaks of 26.46° and 30.11° in Figure 1 show the characteristics of molybdenum (JCPDS No. 98-009-0157) and the 2θ peak of 43.03° indicates the characteristics of molybdenum phosphide (JCPDS No. 89-5110). It was relatively consistent with similar studies on MoP catalysts (Alvarez-Galvan et al., 2019; Carencio et al., 2013).

SEM-EDX analysis aims to see the morphological differences between the surface of Na-Bentonite and molybdenum phosphide pillared bentonite. Figure 2 shows the surface of the catalyst using a magnification of 5000 times.

It can be seen from Figure 2 that Na-Bentonite has a layered surface that forms a thin line and the aggregate mass of the irregularly shaped particles in the form of agglomerates (Bendou & Amrani, 2014), while MoP-Bentonite has many gaps and is covered by a small oval-shaped spot indicating the presence of molybdenum phosphide. Pillarization will change the morphological properties of the catalyst (Bertella & Pergher, 2017), and constituent atomic element changes in the catalyst can be observed using EDX.

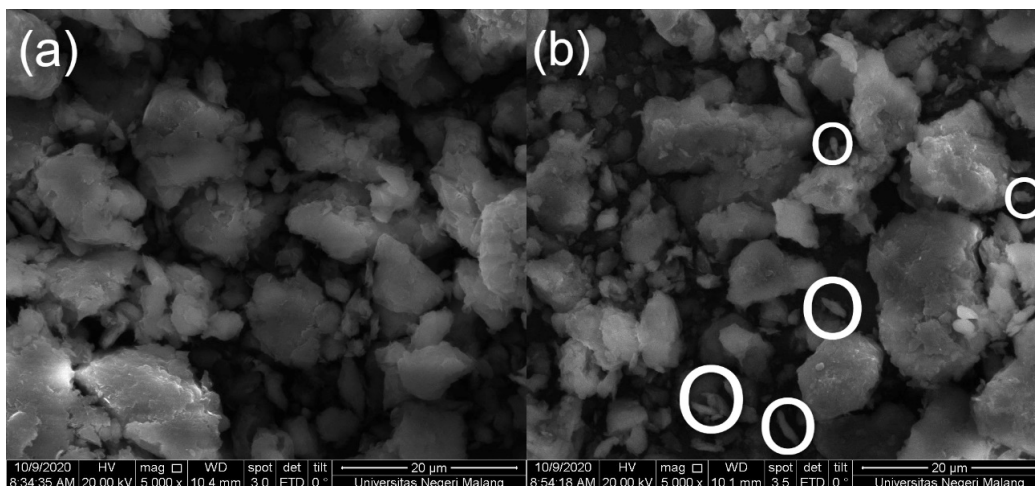


Figure 2. The surface morphology of (a) Na-Bentonite and (b) MoP-Bentonite catalyst

The results of EDX analysis can be seen in Table 2, which shows the change in the percentage of atoms of several elements. Table 2 shows an increase of Mo and P elements from 0 to 5.05% and 0.24 to 0.80%, respectively, as well as decreasing content in other cations. The change in atomic percent of several elements is due to the presence of molybdenum phosphide, which replaces these elements in the interlayer and indicates that the pillarization was successfully done. A similar finding has been reported by Harun et al. (2016) in the study of the modification of montmorillonite.

Table 2
Analysis of catalyst elements content using EDX analysis

Elements	Na-Bentonite (% of atoms)	MoP-Bentonite (% of atoms)
C	13.92	24.91
O	46.05	42.63
Na	2.49	1.59
Mg	3.25	1.69
Al	8.47	5.33
Si	21.12	16.09
Ca	0.55	-
Fe	3.46	1.92
P	0.24	0.80
Mo	-	5.03

Figure 3 shows the gas sorption analysis of Na-Bentonite and MoP-Bentonite using a gas sorption analyzer (GSA) through nitrogen adsorption-desorption. The surface area, pore volume, and diameter volume of catalyst were obtained through calculations using the BET equation as shown in Table 3.

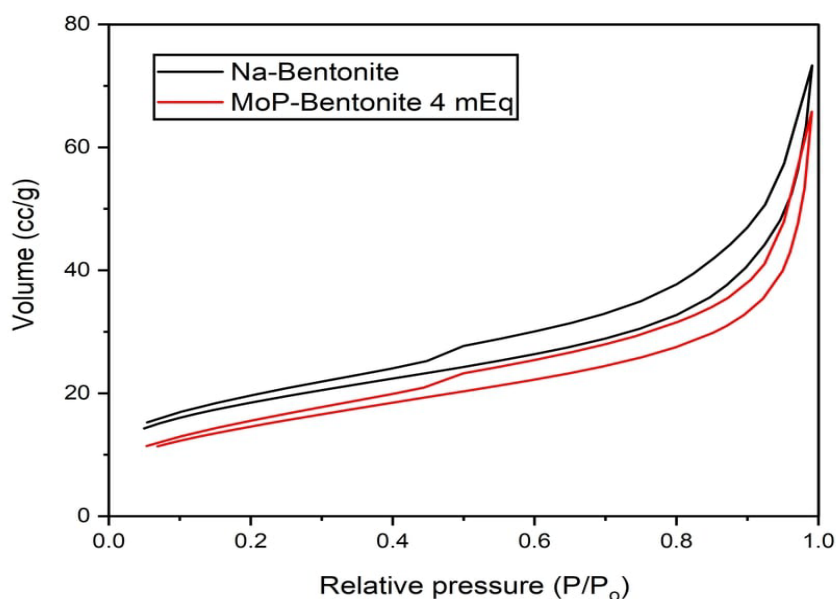


Figure 3. N_2 adsorption-desorption of Na-Bentonite and MoP-Bentonite catalyst

Table 3

BET calculations of Na-Bentonite and MoP-Bentonite catalyst

Catalyst	Surface Area (m^2/g)	Pore Volume (cc/g)	Pore Diameter (\AA)
Na-Bentonite	52.84	0.07103	53.76
MoP-Bentonite	63.69	0.10180	63.93

The adsorption-desorption isotherms for Na-Bentonite and MoP-Bentonite show isotherms of type II, usually found in solids with pores or macropores (Petrović et al., 2014), while the hysteresis loop show type C, which has a steeper desorption curve than adsorption. This type usually occurs in pores and gaps such as two parallel plate slits. This type indicates that Na-Bentonite and MoP-Bentonite have large gaps or large pores (Thommes et al., 2015). Table 3 shows an increase in the surface area of the catalyst after pillarization of about 20% compared to Na-Bentonite. An increase in surface area is also

positively correlated with increased pore volume and diameter, which are characteristics of pillared bentonite (Bertella & Pergher, 2017). The increase of the pores is probably due to the substitution of Mo into the silica framework. Mo-O-Si bonds are longer than Si-O-Si, which leads to pore expansion (Liu et al., 2016). The increase of surface area, pore volume, and pore diameter indicate that the pillarization using MoP has been successfully done. A similar finding has also been reported by Hamza et al. (2015) in the study of bentonite modification using Ti and Fe.

The acidity of the catalyst is an important property in catalytic reactions. The catalytic activity is affected by the surface concentration of the acid site, including the strength of the acid (Viftaria et al., 2019). The total acidity analysis of Na-Bentonite and MoP-Bentonite Catalyst using Gravimetric Method is shown in Table 4.

The increase of acidity after pillarization occurred due to MoP-Bentonite having more Lewis acid site and the larger pore, which adsorbed more ammonia than Na-Bentonite. A similar finding was reported by Caglar et al. (2015) bentonite pillarization could increase the surface acidity and catalytic property. MoP-Bentonite 4 mEq/g has the highest increase in acidity from 1.5755 to 5.7732 mmol/g, and this indicates the increase of the catalytic activity. It is proven that through GC-MS analysis, the highest DIPE yield was obtained at a catalyst concentration of 4 mEq/g. However, when the concentration of Mo⁶⁺ metal exceeds 4 mEq/g, the acidity of the catalyst relatively decreases; this may be due to the formation of aggregates or agglomerates that can block the acid site leading to a decrease in the acidity of the catalyst (Argyle & Bartholomew, 2015).

Table 4

Total acidity analysis of catalyst using gravimetric method

Catalysts	Total acidity (mmol / gram)
Na-Bentonite	1.5755
MoP-Benonite 2 mEq/g	3.9270
MoP-Benonite 4 mEq/g	5.7732
MoP-Benonite 6 mEq/g	4.1563
MoP-Benonite 8 mEq/g	5.1488

Isopropyl Alcohol Dehydration Conversion

Isopropyl alcohol was converted to DIPE by dehydration using Na-Bentonite and MoP-Bentonite as a catalyst with open reflux at 160°C for 3.5 hours. The percentage yield of DIPE can be seen in Figure 4.

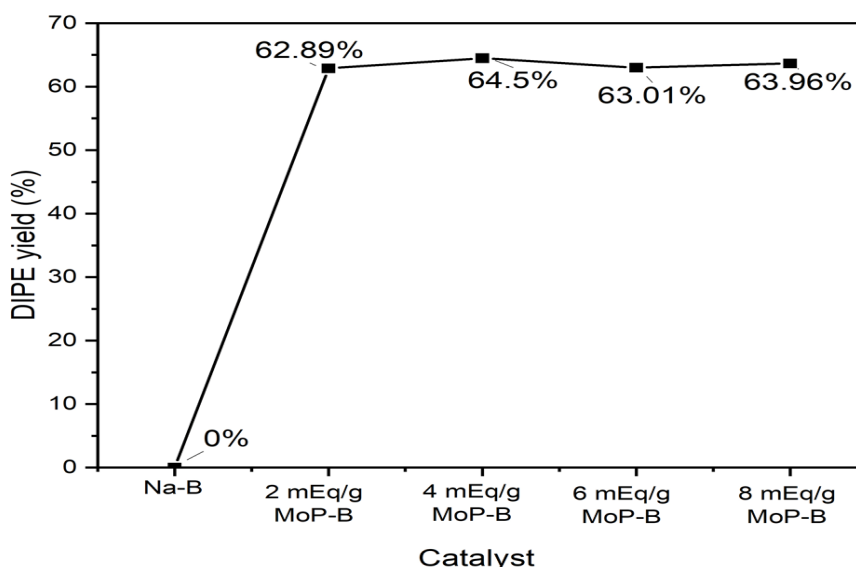


Figure 4. DIPE yield using Na-Bentonite and MoP-Bentonite catalyst

It can be seen in Figure 4 that MoP-bentonite catalysts gave higher DIPE yield than Na-bentonite. It is known that the presence of the catalytic acid site is positively correlated to the increase in the conversion percentage and promotes the dehydration mechanism (Armenta et al., 2019). Compared to Na-bentonite, the Mo metal in MoP-bentonite has a half-empty d orbital act as an active site of Lewis acid (Gao et al., 2021) which can play a role in isopropyl alcohol dehydration catalysis, and this will lead to an increase in DIPE conversion, significantly. Furthermore, the percentage of DIPE conversion increased from 2 to 4 mEq of catalyst concentration; surprisingly, the percentage of DIPE relatively gave the constant conversion when the catalyst concentration was more than 4 mEq. It can be observed that with a relatively small concentration, Mo^{6+} metal can be pillared in the bentonite interlayer evenly. However, suppose the concentration is too large. In that case, the Mo^{6+} metal will likely form aggregates or lumps, reducing the acid site, thus causing the percentage of DIPE conversion relatively to constant (Argyle & Bartholomew, 2015). The catalytic activity of MoP-bentonite in this study resulted in a relatively higher percentage of DIPE conversion of 64.50% compared to the catalyst of Fe_3O_4 -CuO impregnated alumina (53%) (Armenta et al., 2019), AlPO_4 -650 (16%) (Blanco-Bonilla et al., 2016), xSi-Zr (0%) (Pyen et al., 2018), and CuP (0%) (Ouchabi et al., 2016).

CONCLUSION

Synthesis of molybdenum phosphide pillared bentonite (MoP-Bentonite) catalysts has been conducted with variations of MoP-Bentonite concentrations of 2, 4, 6, and 8 mEq/g. The catalysts were used for the dehydration of isopropyl alcohol to produce the diisopropyl ether (DIPE). The characterization showed that the pillarization of bentonite using molybdenum phosphide had been successfully synthesized and inherently increased the surface area, pore-volume, diameter volume, and total acidity of the Na-Bentonite catalyst. The highest yield of DIPE product formed using 4 mEq/g MoP-Bentonite catalysts and gave the highest total acidity compared to Na-Bentonite and other catalysts. The MoP-Bentonite catalyst showed good catalytic activity for DIPE production.

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