Dehydration Isopropyl Alcohol to Diisopropyl Ether over Molybdenum Phosphide Pillared Bentonite

by Hasanudin Hasanudin

Submission date: 06-Apr-2022 05:42AM (UTC+0700)
Submission ID: 1802820954
File name: Artikel_Jurnal_JST_30_2_2022.pdf (1.35M)
Word count: 6195
Character count: 33961

Pertanika J. Sci. & Technol. 30 (2): 1739 - 1754 (2022)

PERTANIKA JOURNALS

SCIENCE & TECHNOLOGY

Journal homepage: http://www.pertanika.upm.edu.my/

Dehydration Isopropyl Alcohol to Diisopropyl Ether over Molybdenum Phosphide Pillared Bentonite

Hasanudin Hasanudin[1,2]*, Wan Ryan Asri[1], Kristina Tampubolon[1], Fahma Riyanti[1], Widia Purwaningrum[1] and Karna Wijaya[3]

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

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

[3]*Department 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 Mo^{6+} 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

ARTICLE INFO

Article history:
Received: 27 October 2021
Accepted: 19 January 2022
Published: 31 March 2022

DOI: https://doi.org/10.47836/pjst.30.2.47

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 (Widya Purwaningrum)
karnawijaya@ugm.ac.id (Karna Wijaya)
*Corresponding author

ISSN: 0128-7680
e-ISSN: 2231-8526

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 Fe_3O_4/γ-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). Mo^{6+} 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 Mo^{6+} 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 $AgNO_3$. $AgNO_3$ 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 $[Cu(en)_2]^{2+}$. 3. 98g 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 $[Cu(en)_2]^{2+}$. 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 $[Cu(en)_2]^{2+}$, such as 6 x 10^{-3}, 7 x 10^{-3}, 8 x 10^{-3}, 9 x 10^{-3}, and 10 x 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 $(NH_4)_2HPO_4$ solution at a 1 mL/minute rate with the volume of molar ratio Mo:P = 1:3. Next, an amount of 10 mL of 0.5 M $(NH_4)_2HPO_4$ 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 $(NH_4)_2HPO_4$ 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 Hosseininejad 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 A), 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 Mo^{6+} metal (Mnasri-Ghnimi & Frini-Srasra, 2014). This trend was consistent with a previous report (Kıpçak & Kalpazan, 2020). The greater the CEC value, the more Mo^{6+} 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°

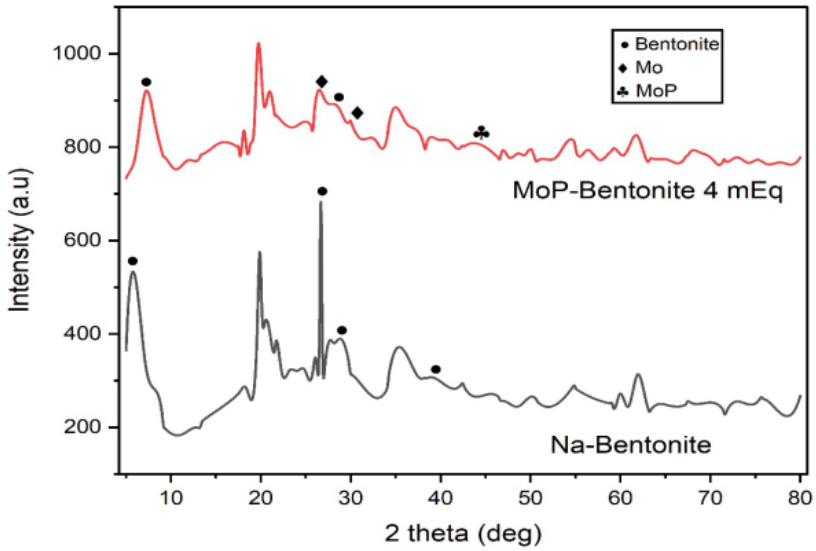

Figure 1. X-ray diffractogram of Na-Bentonite and MoP-Bentonite catalyst

(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; Carenco 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.

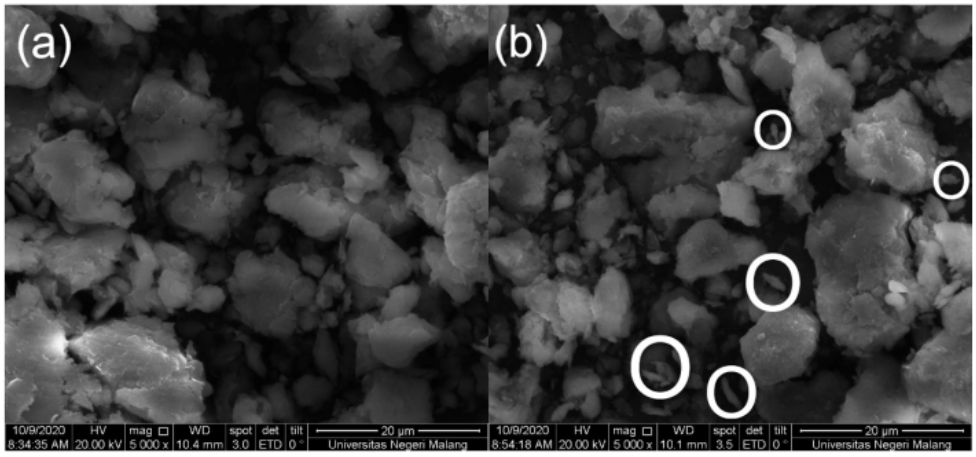

Figure 2. The surface morphology of (a) Na-Bentonite and (b) MoP-Bentonite catalyst

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.

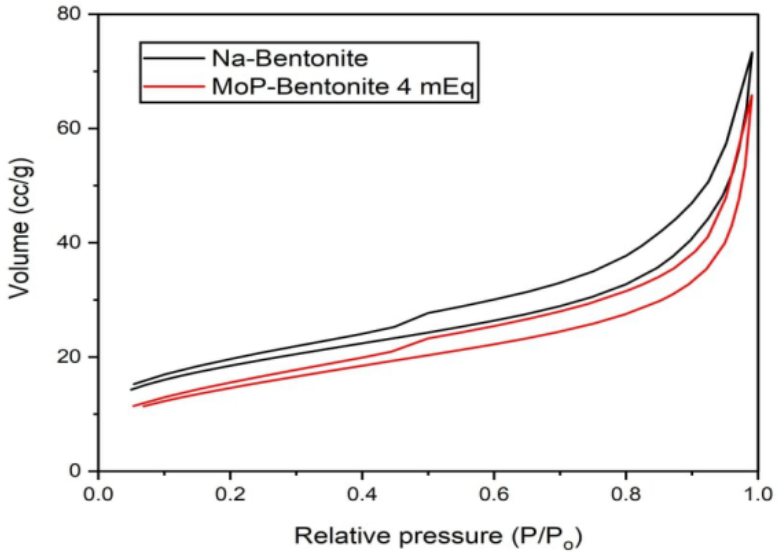

Figure 3. N_2 adsorption-desorption of Na-Bentonite and MoP-Bentonite catalyst

Table 3

BET calculations of Na-Bentonite and MoP-Bentonite catalyst

Catalyst	Surface Area (m^2/g)	Pore Volume (cc/g)	Pore Diameter (Å)
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 (Vifttaria 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 Mo^{6+} 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.

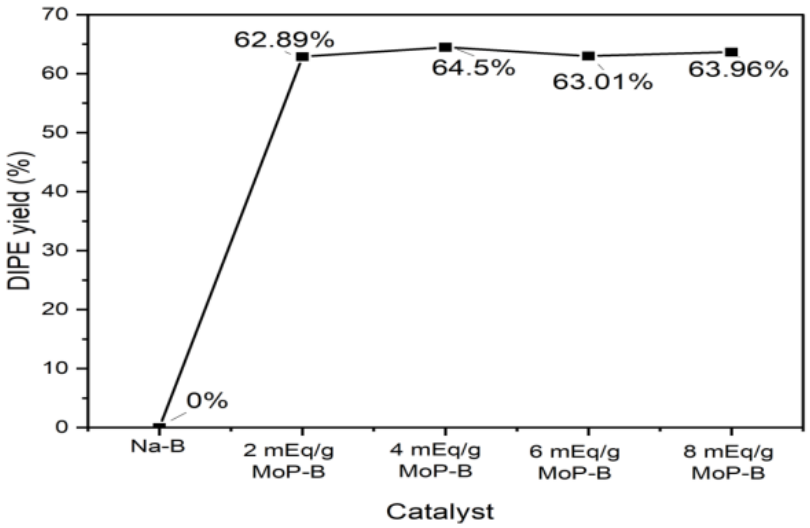

Figure 4. DIPE yield using Na-Bentonite and MoP-Bentonite catalyst

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.

ACKNOWLEDGEMENTS

The financial support by The LPPM Universitas Sriwijaya under Hibah Kompetitif scheme research grant 2021 number 0010/UN9/SK.LP2M.PT/2021 is gratefully acknowledged.

REFERENCES

Ahmadi, S., & Almasi, M. (2020). Experimental and modeling study of diisopropyl ether and 2-alkanol; PC-SAFT model and free volume theory. *Journal of Chemical Thermodynamics*, *142*, Article 106025. https://doi.org/10.1016/j.jct.2019.106025

Ahmed, A. A., Saaid, I. M., Akhir, N. A. M., & Rashedi, M. (2016). Influence of various cation valence, salinity, pH and temperature on bentonite swelling behaviour. *AIP Conference Proceedings*, *1774*(1), Article 040005. https://doi.org/10.1063/1.4965087

Akkouche, A., Benmounah, A., Gueciouer, A., & Chalah, K. (2020). Valorization of mixed metal hydroxide on Algerian Na-Bentonite suspensions: Application to water-based drilling fluid. *Egyptian Journal of Petroleum*, *29*(2), 127-131. https://doi.org/10.1016/j.ejpe.2019.12.005

Al-Arkawazi, S. A. F. (2019). The gasoline fuel quality impact on fuel consumption, air-fuel ratio (AFR), lambda (λ) and exhaust emissions of gasoline-fueled vehicles. *Cogent Engineering*, *6*(1), Article 1616866. https://doi.org/10.1080/23311916.2019.1616866

Alvarez-Galvan, M. C., Campos-Martin, J. M., & Fierro, J. L. G. (2019). Transition metal phosphides for the catalytic hydrodeoxygenation of waste oils into green diesel. *Catalysts*, *9*(3), Article 293. https://doi.org/10.3390/catal9030293

Argyle, M. D., & Bartholomew, C. H. (2015). Heterogeneous catalyst deactivation and regeneration: A review. *Catalysts*, *5*(1), 145-269.

Armenta, M. A., Valdez, R., Silva-Rodrigo, R., & Olivas, A. (2019). Diisopropyl ether production via 2-propanol dehydration using supported iron oxides catalysts. *Fuel*, *236*, 934-941. https://doi.org/10.1016/j.fuel.2018.06.138

Aziz, B. K., Salh, D. M., Kaufhold, S., & Bertier, P. (2019). The high efficiency of anionic dye removal using Ce-Al13/pillared clay from Darbandikhan natural clay. *Molecules*, *24*(15), Article 2720. https://doi.org/10.3390/molecules24152720

Belousov, P., Semenkova, A., Egorova, T., Romanchuk, A., Zakusin, S., Dorzhieva, O., Tyupina, E., Izosimova, Y., Tolpeshta, I., Chernov, M., & Krupskaya, V. (2019). Cesium sorption and desorption on glauconite, bentonite, zeolite, and diatomite. *Minerals*, *9*(10), Article 625. https://doi.org/10.3390/min9100625

Bendou, S., & Amrani, M. (2014). Effect of hydrochloric acid on the structural of sodic-bentonite clay. *Journal of Minerals and Materials Characterization and Engineering, 2*(5), Article 49867. https://doi.org/10.4236/jmmce.2014.25045

Bertella, F., & Pergher, S. B. C. (2017). Reuse of pillaring agent in sequential bentonite pillaring processes. *Materials*, *10*(7), Article 705. https://doi.org/10.3390/ma10070705

Blanco-Bonilla, F., Lopez-Pedrajas, S., Luna, D., Marinas, J. M., & Bautista, F. M. (2016). Vanadium oxides supported on amorphous aluminum phosphate: Structural and chemical characterization and catalytic performance in the 2-propanol reaction. *Journal of Molecular Catalysis A: Chemical*, *416*, 105-116. https://doi.org/10.1016/j.molcata.2016.02.026

Caglar, B., Cubuk, O., Demir, E., Coldur, F., Catir, M., Topcu, C., & Tabak, A. (2015). Characterization of AlFe-pillared Unye bentonite: A study of the surface acidity and catalytic property. *Journal of Molecular Structure*, *1089*, 59-65. https://doi.org/10.1016/j.molstruc.2015.02.034

Carenco, S., Portehault, D., Boissière, C., Mézailles, N., & Sanchez, C. (2013). Nanoscaled metal borides and phosphides: Recent developments and perspectives. *Chemical Reviews*, *133*(10), 7981-8065.

Chan, X., Akter, N., Yang, P., Ooi, C., James, A., Boscoboinik, J. A., Parise, J. B., & Kim, T. (2019). Fundamental study of furfuryl alcohol dehydration reaction over molybdenum oxide catalyst. *Molecular Catalysis*, *466*, 19-25. https://doi.org/10.1016/j.mcat.2019.01.011

Cheng, R., Shu, Y., Li, L., Zheng, M., Wang, X., Wang, A., & Zhang, T. (2007). Synthesis and characterization of high surface area molybdenum phosphide. *Applied Catalysis A: General*, *316*(2), 160-168. https://doi.org/10.1016/j.apcata.2006.08.036

Deng, C., Ding, F., Li, X., Guo, Y., Ni, W., Yan, H., Sun, K., & Yan, Y. M. (2015). Templated-preparation of a three-dimensional molybdenum phosphide sponge as a high performance electrode for hydrogen evolution. *Journal of Materials Chemistry A*, *4*(1), 59-66. https://doi.org/10.1039/c5ta05453b

Fan, X., Sun, W., Liu, Z., Gao, Y., Yang, J., Yang, B., & Law, C. K. (2021). Exploring the oxidation chemistry of diisopropyl ether: Jet-stirred reactor experiments and kinetic modeling. *Proceedings of the Combustion Institute*, *38*(1), 321-328. https://doi.org/10.1016/j.proci.2020.06.242

Gao, H., Hu, L., Hu, Y., Lv, X., Wu, Y. B., & Lu, G. (2021). Origins of Lewis acid acceleration in nickel-catalysed C–H, C–C and C–O bond cleavage. *Catalysis Science & Technology*, *11*(13), 4417-4428. https://doi.org/10.1039/D1CY00660F

Hamza, W., Chtara, C., & Benzina, M. (2015). Characterization and application of Fe and iso-Ti-pillared bentonite on retention of organic matter contained in wet industrial phosphoric acid (54%): Kinetic study. *Research on Chemical Intermediates*, *41*(9), 6117-6140. https://doi.org/10.1007/s11164-014-1726-2

Harun, F. W., Almadani, E. A., & Radzi, S. M. (2016). Metal cation exchanged montmorillonite K10 (MMT K10): Surface properties and catalytic activity. *Journal of Scientific Research and Development*, *3*(3), 90-96.

Hasanudin, H., Rachmat, A., Said, M., & Wijaya, K. (2020). Kinetic model of crude palm oil hydrocracking over Ni/Mo ZrO_2–pillared bentonite catalyst. *Periodica Polytechnica Chemical Engineering*, *64*(2), 238-247. https://doi.org/10.3311/PPch.14765

Hayakawa, T., Oya, M., Minase, M., Fujita, K. ichi, Teepakakorn, A. (Pleng), & Ogawa, M. (2019). Preparation of sodium-type bentonite with useful swelling property by a mechanochemical reaction from a weathered bentonite. *Applied Clay Science*, *175*, 124-129. https://doi.org/10.1016/j.clay.2019.04.009

Hosseininejad, S., Afacan, A., & Hayes, R. E. (2012). Catalytic and kinetic study of methanol dehydration to dimethyl ether. *Chemical Engineering Research and Design*, *90*(6), 825-833. https://doi.org/10.1016/j.cherd.2011.10.007

Kashyap, P., Gahlyan, S., Rani, M., Tiwari, D. P., & Maken, S. (2020). Thermophysical properties of ternary liquid mixture of diisopropyl ether (1) + ethanol (2) + n-heptane (3): Measurement and correlation. *Journal of Molecular Liquids*, *319*(1), Article 114219. https://doi.org/10.1016/j.molliq.2020.114219

Kıpçak, İ., & Kalpazan, E. (2020). Preparation of CoB catalysts supported on raw and Na-exchanged bentonite clays and their application in hydrogen generation from the hydrolysis of NaBH4. *International Journal of Hydrogen Energy*, *45*(50), 26434-26444. https://doi.org/10.1016/j.ijhydene.2020.03.230

Li, P., Lu, Y., & Wang, J. (2020). The effects of fuel standards on air pollution: Evidence from China. *Journal of Development Economics*, *146*, Article 102488. https://doi.org/10.1016/j.jdeveco.2020.102488

Liu, Q., Li, J., Zhao, Z., Gao, M., Kong, L., Liu, J., & Wei, Y. (2016). Synthesis, characterization, and catalytic performances of potassium-modified molybdenum-incorporated KIT-6 mesoporous silica catalysts for the selective oxidation of propane to acrolein. *Journal of Catalysis*, *344*, 38-52. https://doi.org/10.1016/j.jcat.2016.08.014

Mara, A., Wijaya, K., Trisunaryati, W., & Mudasir. (2016). Effect of sulfuric acid concentration of bentonite and calcination time of pillared bentonite. *AIP Conference Proceedings*, *1725*(1), Article 020042. https://doi.org/10.1063/1.4945496

Mnasri-Ghnimi, S., & Frini-Srasra, N. (2014). Promoting effect of cerium on the characteristic and catalytic activity of Al, Zr, and Al-Zr pillared clay. *Applied Clay Science, 88-89*, 214-220. https://doi.org/10.1016/j.clay.2013.10.030

Mnasri, S., Hamdi, N., Frini-Srasra, N., & Srasra, E. (2017). Acid-base properties of pillared interlayered clays with single and mixed Zr-Al oxide pillars prepared from Tunisian-interstratified illite-smectite. *Arabian Journal of Chemistry*, *10*(8), 1175-1183. https://doi.org/10.1016/j.arabjc.2014.07.004

Muñoz-Rujas, N., Bazile, J. P., Aguilar, F., Galliero, G., Montero, E., & Daridon, J. L. (2017). Speed of sound, density and derivative properties of diisopropyl ether under high pressure. *Fluid Phase Equilibria*, *449*, 148-155. https://doi.org/10.1016/j.fluid.2017.06.024

Ouchabi, M., Baalala, M., Elaissi, A., & Bensitel, M. (2016). Effect of calcination temperature on the structure of copper orthophosphates and their catalytic activity in the decomposition of 2-propanol. *Journal of Materials and Environmental Science*, *7*(4), 1417-1424.

Pyen, S., Hong, E., Shin, M., Suh, Y. W., & Shin, C. H. (2018). Acidity of co-precipitated SiO_2-ZrO_2 mixed oxides in the acid-catalyzed dehydrations of iso-propanol and formic acid. *Molecular Catalysis*, *448*, 71-77. https://doi.org/10.1016/j.mcat.2018.01.031

Petrović, Z., Dugić, P., Aleksić, V., Vojislav, S., Sadadinović, J., Mićić, V., & Kljajić, N. (2014). Composition, structure and textural characteristics of domestic acid activated bentonite. *Contemporary Materials*, *1*(5), 133-139. https://doi.org/10.7251/cm.v1i5.1509

Rinaldi, N., & Kristiani, A. (2017). Physicochemical of pillared clays prepared by several metal oxides. *AIP Conference Proceedings*, *1823*(1), Article 020063. https://doi.org/10.1063/1.4978136

Ruddy, D. A., Schaidle, J. A., Ferrell, J. R., Wang, J., Moens, L., & Hensley, J. E. (2014). Recent advances in heterogeneous catalysts for bio-oil upgrading via "ex situ catalytic fast pyrolysis": Catalyst development through the study of model compounds. *Green Chemistry*, *16*(2), 454-490. https://doi.org/10.1039/c3gc41354c

Said, A. E. A. A., El-Wahab, M. M. A., & El-Aal, M. A. (2014). The catalytic performance of sulfated zirconia in the dehydration of methanol to dimethyl ether. *Journal of Molecular Catalysis A: Chemical*, *394*, 40-47. https://doi.org/10.1016/j.molcata.2014.06.041

Shao, H., Gao, W., Zhang, D., Liu, Z., & Li, W. (2013). Study on treatment effect of three types of industrial wastewater by ammonium molybdate-modified bentonite. *Advanced Materials Research*, *634*, 286-291. https://doi.org/10.4028/www.scientific.net/AMR.634-638.286

Sun, Y., Jiu, H., Tian, J., Zhang, L., Han, T., Guo, F., & Qiu, M. (2020). Preparation of molybdenum phosphide nanoparticles/nitrogen-phosphorus co-doped carbon nanosheet composites for efficient hydrogen evolution reaction. *Journal of Solid State Chemistry*, *284*, Article 121182. https://doi.org/10.1016/j.jssc.2020.121182

Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J. P., Rodriguez-Reinoso, F., Rouquerol, J., & Sing, K. S. W. (2015). Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure and Applied Chemistry*, *87*(9-10), 1051-1069. https://doi.org/10.1515/pac-2014-1117

Totong, S., Daorattanachai, P., Laosiripojana, N., & Idem, R. (2020). Catalytic depolymerization of alkaline lignin to value-added phenolic-based compounds over Ni/CeO_2-ZrO_2 catalyst synthesized with a one-step chemical reduction of Ni species using NaBH4 as the reducing agent. *Fuel Processing Technology*, *198*, Article 106248. https://doi.org/10.1016/j.fuproc.2019.106248

Uyumaz, A., Aydoğan, B., Calam, A., Aksoy, F., & Yılmaz, E. (2020). The effects of diisopropyl ether on combustion, performance, emissions and operating range in a HCCI engine. *Fuel*, *265*, Article 116919. https://doi.org/10.1016/j.fuel.2019.116919

Vifttaria, M., Nurhayati, N., & Anita, S. (2019). Surface acidity of sulfuric acid activated maredan clay catalysts with Boehm titration method and pyridine adsorption-FTIR. *Journal of Physics: Conference Series*, *1351*(1), Article 012040. https://doi.org/10.1088/1742-6596/1351/1/012040

Wang, C., Jia, M., Bai, Z., Shi, M., Chen, X., Fan, J., & Dai, F. (2020). The separation of isopropyl alcohol from diisopropyl ether system using glycols: Phase equilibrium and rigorous correlation. *Journal of Chemical Thermodynamics*, *150*, Article 106230. https://doi.org/10.1016/j.jct.2020.106230

Wu, Z., Song, M., Zhang, Z., Wang, J., & Liu, X. (2019). Various strategies to tune the electrocatalytic performance of molybdenum phosphide supported on reduced graphene oxide for hydrogen evolution reaction. *Journal of Colloid and Interface Science*, *536*, 638-645. https://doi.org/10.1016/j.jcis.2018.10.068

Zaghouane-Boudiaf, H., Boutahala, M., Sahnoun, S., Tiar, C., & Gomri, F. (2014). Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing the 2,4,5-trichlorophenol. *Applied Clay Science*, *90*, 81-87. https://doi.org/10.1016/j.clay.2013.12.030

Zhu, L., Cheung, C. S., Zhang, W. G., & Huang, Z. (2011). Combustion, performance and emission characteristics of a di diesel engine fueled with ethanol-biodiesel blends. *Fuel*, *90*(5), 1743-1750. https://doi.org/10.1016/j.fuel.2011.01.024

Dehydration Isopropyl Alcohol to Diisopropyl Ether over Molybdenum Phosphide Pillared Bentonite

ORIGINALITY REPORT

13%	8%	10%	3%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	Submitted to Sriwijaya University Student Paper	2%
2	Desnelli, W R Asri, Hasanudin, M Said, P L Hariani. "Removal of Congo Red and Procion Red Using Zn/Fe Pillared Bentonite", IOP Conference Series: Earth and Environmental Science, 2021 Publication	1%
3	pp.bme.hu Internet Source	1%
4	www.pertanika.upm.edu.my Internet Source	<1%
5	Submitted to The Hong Kong Polytechnic University Student Paper	<1%
6	cyberleninka.org Internet Source	<1%
7	www.science.gov Internet Source	<1%
8	M.A. Armenta, R. Valdez, R. Silva-Rodrigo, A. Olivas. "Diisopropyl ether production via 2-	<1%

propanol dehydration using supported iron oxides catalysts", Fuel, 2019
Publication

9	link.springer.com Internet Source	<1 %
10	Submitted to Universitas Islam Indonesia Student Paper	<1 %
11	Yu Sun, Hongfang Jiu, Jiao Tian, Lixin Zhang, Tao Han, Fengbo Guo, Minyang Qiu. "Preparation of molybdenum phosphide nanoparticles/nitrogen-phosphorus co-doped carbon nanosheet composites for efficient hydrogen evolution reaction", Journal of Solid State Chemistry, 2020 Publication	<1 %
12	engj.org Internet Source	<1 %
13	psasir.upm.edu.my Internet Source	<1 %
14	Menglin Ding, Shufeng Zuo, Chenze Qi. "Preparation and characterization of novel composite AlCr-pillared clays and preliminary investigation for benzene adsorption", Applied Clay Science, 2015 Publication	<1 %
15	www.ncbi.nlm.nih.gov Internet Source	<1 %

16	Bart Hermans, Frans C. De Schryver, Jan van Stam, Noeel Boens et al. "Global Compartmental Analysis of the Fluorescence Decay Surface of the Halato Telechelic Polymer (N,N-Dimethyl-N-[3-(1-pyrenyl)propyl]ammonio)trifluoromethanesulfonate-End-Capped Poly(tetrahydrofuran)", Macromolecules, 2002 Publication	<1 %
17	www.freepatentsonline.com Internet Source	<1 %
18	A. E. El-Gendy, M. G. El-Bardicy, H. M. Loutfy, M. F. El-Tarras. "STABILITY INDICATING METHOD FOR THE DETERMINATION OF NIZATIDINE USING 3-METHYL-2-BENZOTHIAZOLINONE HYDRAZONE", Spectroscopy Letters, 2001 Publication	<1 %
19	Benjamin Nyblade, Angela O'Mahony, Aim Sinpeng. "Social Media Data and the Dynamics of Thai Protests", Asian Journal of Social Science, 2015 Publication	<1 %
20	Pei Li, Yi Lu, Jin Wang. "The effects of fuel standards on air pollution: Evidence from China", Journal of Development Economics, 2020 Publication	<1 %
21	jbiochemtech.com Internet Source	<1 %

22	scholarworks.uni.edu Internet Source	<1 %
23	Hosana Aguiar Freitas de Andrade, Nítalo André Farias Machado, Analya Roberta Fernendes Oliveira, Taciella Fernandes Silva et al. "Effect of Substrate of Carnauba Residue with Humic Substances on Seedling Production of Papaya Cultivar 'Golden'", Communications in Soil Science and Plant Analysis, 2022 Publication	<1 %
24	M Vifttaria, Nurhayati, S Anita. "Surface Acidity of Sulfuric Acid Activated Maredan Clay Catalysts with Boehm Titration Method and Pyridine Adsorption-FTIR", Journal of Physics: Conference Series, 2019 Publication	<1 %
25	Robert R Widjaya, Nanda Saridewi, Alda A Putri, Nino Rinaldi, Adid A Dwiatmoko. "Fe-Cr pillared clay as catalysts for the ethanol to gasoline conversion", IOP Conference Series: Materials Science and Engineering, 2021 Publication	<1 %
26	eprints.utm.my Internet Source	<1 %
27	iopscience.iop.org Internet Source	<1 %

28	"Proceedings of the 3rd International Conference on Separation Technology", Springer Science and Business Media LLC, 2021 Publication	<1 %
29	Didier Astruc, Feng Lu, Jaime Ruiz Aranzaes. "Nanoparticles as Recyclable Catalysts: The Frontier between Homogeneous and Heterogeneous Catalysis", Angewandte Chemie International Edition, 2005 Publication	<1 %
30	Halima Gallouze, Djamal-Eddine Akretche, Carla Daniel, Isabel Coelhoso, João G. Crespo. "Removal of Synthetic Estrogen from Water by Adsorption on Modified Bentonites", Environmental Engineering Science, 2021 Publication	<1 %
31	Sana Ghrab, Sébastien Balme, Marc Cretin, Samir Bouaziz, Mourad Benzina. "Adsorption of terpenes from Eucalyptus globulus onto modified beidellite", Applied Clay Science, 2018 Publication	<1 %
32	tsukuba.repo.nii.ac.jp Internet Source	<1 %
33	Hongjuan Liu, Shuibo Xie, Ju Liao, Tianrun Yan, Yingjiu Liu, Xinhai Tang. "Novel graphene oxide/bentonite composite for	<1 %

uranium(VI) adsorption from aqueous solution", Journal of Radioanalytical and Nuclear Chemistry, 2018
Publication

34 Liang Xue, Youhao Liao, Liang Yang, Xiaoping Li, Weishan Li. "Improved rate performance of LiNi0.5Mn1.5O4 cathode for lithium ion battery by carbon coating", Ionics, 2014 <1 %
Publication

35 Qing Yan, Xi Chen, Tong Wei, Guiling Wang, Min Zhu, Yikuan Zhuo, Kui Cheng, Ke Ye, Kai Zhu, Jun Yan, Dianxue Cao, Yiju Li. "Hierarchical Edge-Rich Nickel Phosphide Nanosheet Arrays as Efficient Electrocatalysts toward Hydrogen Evolution in Both Alkaline and Acidic Conditions", ACS Sustainable Chemistry & Engineering, 2019 <1 %
Publication

36 Samira Bendou, Moussa Amrani. "Effect of Hydrochloric Acid on the Structural of Sodic-Bentonite Clay", Journal of Minerals and Materials Characterization and Engineering, 2014 <1 %
Publication

37 repositorio.ufsm.br <1 %
Internet Source

38 worldwidescience.org <1 %
Internet Source

39	www.researchgate.net Internet Source	<1%
40	"Recent Advances in Environmental Science from the Euro-Mediterranean and Surrounding Regions", Springer Nature, 2018 Publication	<1%

Exclude quotes	Off	Exclude matches	Off
Exclude bibliography	On		