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Sulfuric acid-activated Indonesian natural bentonite as solid acid catalysts in microwave-protocol nitrobenzene synthesis

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Original Research

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Abstract:

Research has been conducted on activating Indonesian natural bentonite using sulfuric acid to produce solid acid catalysts for nitrobenzene synthesis in a batch microwave reactor that is in line with green chemistry principles. Indonesian natural bentonite was refluxed with sulfuric acid at various concentrations of 0, 1, 2, 3, and 4 M, followed by calcination with N_2 gas flow to obtain NB, SNB-1, SNB-2, SNB-3, and SNB-4. The results showed that activation of natural bentonite by sulfuric acid can change its phytochemical properties. SNB-2 (sulfated natural bentonite 2 M) is the best catalyst with the highest acidity value compared to other concentration variations. The synthesis of nitrobenzene was carried out in an 800-Watt microwave oven at 60 °C for 2.5 hours with stirring at 600 rpm. We obtained the highest benzene conversion of 33.6% over the SNB-2 catalyst with nitrobenzene selectivity of 100%. Sulfuric acid-activated bentonite has good stability for three consecutive runs, so in the future, we can apply this material as a catalyst candidate for the greener nitrobenzene industry.

Keywords: Bentonite; Microwave-assisted synthesis; Nitrobenzene; Nitration; Sulfuric acid activation

1. Introduction

Nitrobenzene is a nitroaromatic compound widely used to produce various downstream products from benzene-derived compounds. Annual production is estimated at up to 225,000 metric tons [1]. This compound is commonly used in dyes, explosives, agrochemicals, and medicines [2]. In the medicinal field, nitrobenzene is one of the intermediates in the production of paracetamol, a fever-reducing drug widely recognized commercially via the para-aminophenol acylation reaction [3].

On an industrial scale, since the 19th century, nitro groups have been substituted in aromatic compounds such as benzene by mixing sulfuric acid with nitric acid through an exothermic reaction in a batch or continuous reactor [4]. Sulfuric acid in the nitration reaction has a dual function as a homogeneous catalyst and dehydrating agent [5]. Therefore, in such acid mixtures, the amount of sulfuric acid used is always in excess. In this process, sulfuric acid will catalyze the nitration reaction by forming a nitronium cation, as a nitrating agent, from the protonation of nitric acid [6, 7].

This reaction process is included in an efficient response with a high nitrobenzene yield. However, drawbacks arise from using sulfuric acid as a catalyst. The research on benzene or substituted benzene nitration processes has produced many worthwhile advancements, such as improved energy management of contemporary nitration and the exploration of various clean nitration techniques aimed at displacing the use of sulfuric acid [8, 9]. In other words, nitration of aromatic compounds without sulfuric acid would be an appealing alternative. In terms of green chemistry, the synthesis of nitrobenzene by the conventional method is considered less environmentally friendly because using sulfuric acid in the reaction will cause hazardous waste and is difficult to recycle [10]. This reaction can produce water molecules as one of the reaction products, directly causing the formation of dilute sulfuric acid, which cannot be used again for the nitration reaction. Therefore, considerable recovery costs are required to concentrate the dilute sulfuric acid again [11].

Sulfuric acid catalyst also has poor regioselectivity in producing nitrobenzene because sulfuric acid can form bonds with water during the reaction. The sulfuric acid dehydration process can be done adiabatic to minimize this problem [12]. However, increased temperature and mass transfer are required in the adiabatic reaction, so this reaction can lead to undesirable side reactions, such as the formation of nitrophenols, which require many leaching steps that will substantially increase production costs [13]. The high maintenance costs are necessary because the concentrated sulfuric acid homogeneous catalyst can also damage industrial reactors due to its corrosive nature [14].

One of the possible attempts to overcome these problems is to replace sulfuric acid homogeneous catalysts with acid heterogeneous catalysts, one of which is bentonite. Bentonite has long been recognized as an excellent heterogeneous catalyst for several organic reactions because it has a porous structure with a large surface area, good thermal and chemical stability, and is environmentally friendly [15, 16]. The impurity content in natural bentonite can be removed in several ways, one of which is by strong acid treatment such as sulfuric acid. The activation process on bentonite can increase pore volume and the specific surface area of bentonite [17]. The selection of sulfuric acid as a bentonite activating acid in this study is based on previous studies conducted by Amri et al. [18] regarding the performance of H_2SO_4 in activating silica (H_2SO_4/SiO_2) and Saviola et al. [19] on natural zeolite (SNZ-2) so that the catalysts were able to catalyze the synthesis of nitrobenzene with yields of 40.33% and 58.92%, respectively. Based on our short literature review, there has never been a benzene nitration reaction using Indonesian natural bentonite as a solid acid catalyst to substitute sulfuric acid catalyst. In addition, in this study, the synthesis of nitrobenzene was carried out using a batch microwave reactor where the heating losses from conventional methods were replaced with microwave irradiation so that it is claimed to be greener from the principle of reducing energy consumption and reaction time, also lead to higher product yield. The main goal of this research is to reveal a green step in obtaining nitrobenzene as a raw material for paracetamol, thereby creating independence in drug production in the future in line with sustainable development goals.

2. Materials and methods

2.1 Materials

The materials used in this research were natural bentonite obtained from Klaten, Indonesia (CV Fruitanol Energy); sulfuric acid (H_2SO_4 98%, Merck); nitric acid (HNO_3 65%, Merck); benzene (C_6H_6, Smart Lab); sodium sulfate (Na_2SO_4, E Merck); deionized water (CV Bima Aksara Nusa); and N_2 gas (PT Surya Indotim Imex).

2.2 Preparation of natural bentonite

Natural bentonite was washed with deionized water and stirred for 24 hours. Afterward, the mixture was separated by centrifugation at 2000 rpm for 20 minutes. The fine sediment at the top was taken and dried in an oven at 100 ^{o}C for 6 hours. After drying, the solid was ground and sieved with a 200-mesh sieve.

2.3 Activation of natural bentonite using sulfuric acid

As much as 10 g of prepared natural bentonite was then refluxed with sulfuric acid at various concentrations (0, 1, 2, 3, and 4 M) for 2 hours at 60–70 ^{o}C. The solid was washed with deionized water until the pH was neutral and tested for sulfate ions residue with $BaCl_2$. The solid was then oven-dried for 6 h at 100 ^{o}C. Then, the solid was ground and sieved with a 200-mesh sieve. After that, the solid was calcinated with N_2 gas 5 mL/min for 4 h at 500 ^{o}C and labeled as NB, SNB-1, SNB-2, SNB-3, and SNB-4.

2.4 Catalyst characterizations

Fourier Transform Infrared (FTIR) instrument (Thermo Scientific Nicolet iS10) at wavenumbers of 4000–400 cm^{-1} with the KBr pellet technique is used to identify the functional groups in the samples. The change in the Si/Al ratio value of the materials was characterized using the X-ray fluorescence Spectrometer (XRF) instrument (Bruker S2 PUMA). The acidity of the materials was determined using the Temperature Programmed Desorption of Ammonia (NH_3-TPD) instrument (Micromeritrics Chemisorb 2750) with NH_3 desorption was carried out at 100–800 ^{o}C with a heating rate of 10 ^{o}C/min. The mineral content on the materials was identified using the X-ray diffractometer (XRD) instrument (Shimadzu XRD-6000) with a Cu X-ray tube (1.5406 A). The textural properties of the catalyst were characterized using the Surface Area Analyzer (SAA) instrument (Quantachrome Novatouch LX-4) with a degassing temperature of 300 ^{o}C for 4 hours. The morphological structure and elemental content on the surface of the catalyst were studied using the Scanning Electron Microscope-Electron Dispersive X-ray spectrometer (SEM-EDX) instrument (JEOL JED-2300) and Transmission Electron Microscope (TEM) instrument (JEM-1400 JEOL/EO).

2.5 Application of sulfuric acid-activated natural bentonite in the nitrobenzene synthesis

Sulfated natural bentonite (SNB) catalysts were weighed as much as 1.0 g. In this synthesis, a batch microwave reactor (800 Watt) was used, and the scheme of the reactor can be seen in Fig. 1 [19]. The catalyst was mixed with 20 mL of 65% HNO_3 and 15 mL of benzene (HNO_3/benzene = 2.63 mol/mol). The temperature was set at 60 ^oC, and the reaction was run for 2.5 hours. The mixture was stirred at 600 rpm. After the product was obtained, the catalyst was separated by centrifugation, Na_2SO_4 was added to remove water, and the pure nitrobenzene was obtained for analysis by GC-MS. The separated catalyst was then washed with acetone and oven-dried for reuse in the next run. This nitrobenzene synthesis was carried out in three runs using the same catalyst. The benzene conversion and selectivity of the catalyst can be determined using Eq. 1 and Eq. 2, respectively.

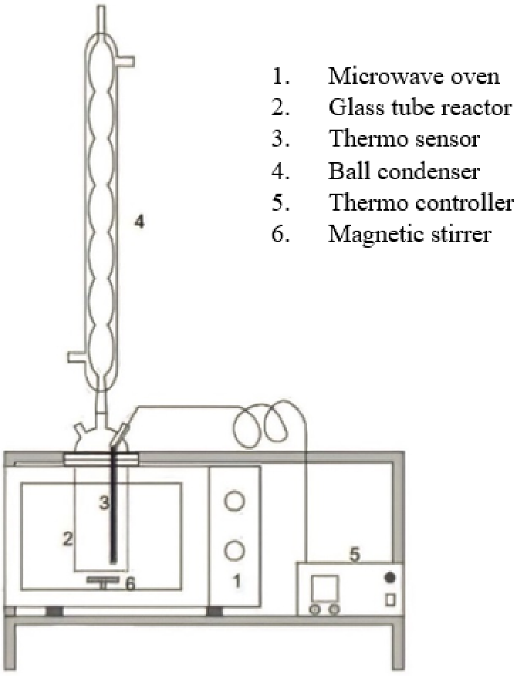

Figure 1. The schematic diagram of the batch microwave reactor.

$$\text{Benzene conversion}(\%) = \frac{V_{\text{nitrobenzene}}(\text{mL}) \times \rho_{\text{nitrobenzene}}(\text{g/mL})}{m_{\text{nitrobenzene}} \text{ with yield } 100\%(\text{g})} \times 100 \quad (1)$$

$$\text{Selectivity}(\%) = \frac{\text{GC area of nitrobenzene}}{\text{total GC area}} \times 100 \quad (2)$$

3. Results and Discussion

3.1 Synthesis of H_2SO_4/bentonite samples

3.1.1 Chemical composition

Based on Table 1, it can be seen that there is a change in the amount of SiO_2 and Al_2O_3 compounds in bentonite after activation with different variations in sulfuric acid concentration. With the increasing concentration of sulfuric acid used, the composition of SiO_2 compounds contained in bentonite increases. In addition, Table 1also shows that natural bentonite also includes a large number of other compounds, such as CaO and Fe_2O_3. The CaO component in natural bentonite is relatively high at 18.90%. However, after sulfuric acid treatment, the CaO component in bentonite drops drastically to 1.4–1.7%. This also happened with the Fe_2O_3 content, which decreased after the sulfuric acid process as the concentration increased.

The Si/Al ratio of the catalyst increases as the concentration of sulfuric acid used increases. This proves that sulfuric acid modification on natural bentonite can increase the amount of silica in the bentonite structure. This result follows the research by Gandhi et al. [16], which states that sulfuric acid modification on bentonite can increase the Si/Al ratio due to the loss of cations in the octahedral structure and Al^{3+} from the internal system of bentonite.

3.1.2 FTIR analysis

Fig. 2 shows the FTIR spectra of natural bentonite and activated bentonite with varying concentrations of sulfuric acid. The absorption at a wavenumber of 470 cm^{-1} shows the bending vibrations of the Si–O–Si group in the tetrahedral layer. Asymmetric stretching vibrations of Si–O–Si are demonstrated at a wavenumber of 1041 cm^{-1} [20]. H–O–H stretching vibrations were identified at a wavenumber of 1637 cm^{-1}. The peak at a wavenumber of 3425 cm^{-1} is identified as bending vibrations of O–H groups. In the NB sample, there is a sharp peak at wavenumber 1430 cm^{-1} and 877 cm^{-1}, one of the impurities found in natural bentonite.

Table 1. Compound composition and Si/Al ratio obtained by XRF.

Composition	NB	SNB-1	SNB-2	SNB-3	SNB-4
SiO_2 (%)	46.81	61.10	62.55	64.06	64.41
Al_2O_3 (%)	19.13	24.40	24.09	23.19	22.76
CaO (%)	18.90	1.71	1.44	1.50	1.75
Fe_2O_3 (%)	7.60	4.49	4.43	3.82	3.79
Other oxides (%)	7.56	8.30	7.49	7.43	7.29
Si (%)	21.87	28.56	29.24	29.94	30.11
Al (%)	10.13	12.91	12.75	12.27	12.05
Si/Al ratio	2.16	2.21	2.29	2.44	2.50

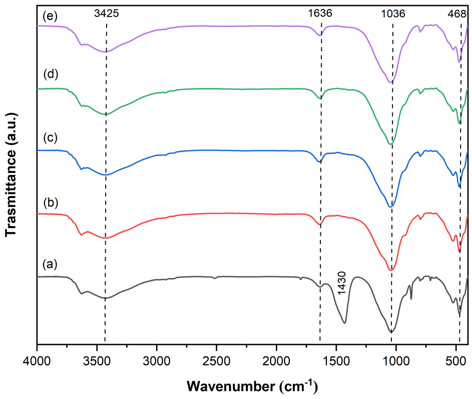

Figure 2. FTIR spectra of (a) NB, (b) SNB-1, (c) SNB-2, (d) SNB-3, and (e) SNB-4. NB =natural bentonite, and SNB= sulfated natural bentonite.

Absorption at wavenumbers ranging from 1430–1458 cm^{-1} indicates the stretching vibrations of the bentonite's C–O bond ($CaCO_3$) [21]. Meanwhile, absorption, which indicates the vibration of Al–Fe^{3+}–OH, is shown at wavenumbers ranging from 875–885 cm^{-1} [22]. After activation with sulfuric acid on natural bentonite, the sharp peak did not appear. This shows the success of the activation process on bentonite, which aims to remove impurities in the bentonite layer structure.

Activating bentonite material with sulfuric acid and removing impurities in bentonite also occur during the dealumination process. Based on the interpretation of the FTIR spectra, there is a change in the wavenumber shift at 1036 cm^{-1}, which increases along with the higher concentration of sulfuric acid used to 1047 cm^{-1}. The absorption intensity in this wavenumber region also slightly increases. This change in wavenumber absorption shows that the bentonite matrix interacts with sulfuric acid, which results in the decrease of Al atoms. Reducing Al^{3+} cations in the tetrahedral structure will increase the Si/Al ratio. This shows that the bentonite activation process with sulfuric acid was successful.

3.1.3 XRD analysis

The mineral content in the material is interpreted by the peaks from the characterization results using the XRD instrument. The XRD diffractogram in Fig. 3 shows peaks at 2θ=19.43 and 26.31°, indicating montmorillonite material contained in bentonite (ICDD 01-074-1976). The peak at 2θ= 35.75° refers to the peak of quartz mineral (SiO_2) (ICDD 01-074-0765). The natural bentonite sample peaks at 2θ=29.14° and 42.91°, indicating $CaCO_3$ (ICDD 01-086-2341) and MgO (ICDD 00-045-0946) as impurities.

After activation with sulfuric acid, there are some differences in the peaks on the diffractogram of sample SNB-2. The sharp peak at 2θ=29.14° from Fig. 3(a) does not appear in the SNB-2 sample, which indicates that the $CaCO_3$ mineral has dissolved in the activation process with sulfuric acid. The peak at 2θ=42.91°, which is MgO, also did not appear on the activated bentonite catalyst. The intensity of the activated bentonite diffractogram Fig. 3(b) shows an increase compared to Fig. 3(a). This result indicates that after activation with sulfuric acid, the mineral composition of montmorillonite increased due to the loss of impurity ions found in bentonite.

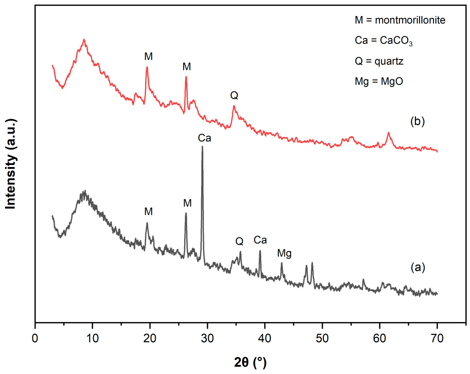

Figure 3. XRD patterns of (a) NB and (b) SNB-2.

3.1.4 Textural properties

Table 2 shows an increase in specific, external, and micropore surface area and total pore and micropore volume in bentonite after activation with sulfuric acid. The increase in surface area and pore volume indicates that the bentonite activation process with sulfuric acid was successful. The activation of bentonite will increase the surface area with cation exchange between bentonite layers. The activation process with sulfuric acid on bentonite also affects its porous volume. In the activation process with sulfuric acid, metal oxides that cover the pores in bentonite are removed so that the pore volume increases after activation. In contrast, decreasing the average pore diameter of sulfuric acid-activated bentonite material is due to the enormous contribution of new micro-dimensional pores that dominate the current bentonite structure.

Fig. 4 shows that natural bentonite and sulfuric acid-

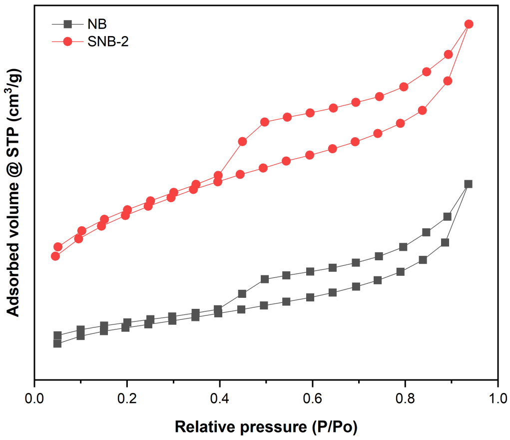

Figure 4. N_2 adsorption-desorption isotherm curves.

Table 2. Textural properties analysis results.

Sample	Specific surface area (m^2/g)	External surface area (m^2/g)[a]	Micropore area (m^2/g)	Total pore volume (m^3/g)	Micropore volume (m^3/g)[a]	Average pore diameter (nm)
NB	35	31	4	0.06	0.0017	6.5
SNB-2	107	63	43	0.10	0.0212	3.9

[a] calculated by t-plot method

activated bentonite samples follow the type IV adsorption-desorption isotherm curve. This type IV isotherm pattern indicates mesoporous material is formed with 2–50 nm dimension based on the IUPAC agreement. The N_2 adsorption-desorption pattern on activated bentonite shows a more dominant mesopore formation, as evidenced by the increase in adsorption with the relative pressure P/P_o. Both curves form H_4-type hysteresis loops that indicate the formation of non-uniform mesoporous materials due to more dominant micropores [23].

3.1.5 Morphological analysis by SEM and TEM

Fig. 5(a) shows natural bentonite has an uneven surface morphology and large particle size. This indicates that the surface area of the natural bentonite catalyst is low. As is typical of montmorillonite, the surface morphology of natural bentonite also exhibits thin, wavy layers with relatively constricted pores [24]. In Fig. 5(b), 2 M sulfuric acid-activated natural bentonite shows a hollow surface morphology and a reduction in particle size. The formation of new pores during the bentonite activation process leads to an overall increase in pore volume and surface area of the material.

Fig. 6(a) shows that bentonite material has a layer structure. The arrangement of aluminosilicate layers in bentonite is held together by the Van der Waals force of attraction [25]. The layer structure is still visible after activation with sulfuric acid. Fig. 6(b) shows that the activation process with sulfuric acid does not change the arrangement of the layers on bentonite. However, there are differences between the two images, namely the presence of light-dark patterns in both samples. Dark patterns and thick lines indicate the aluminosilicate layer, while bright patterns indicate pores on the bentonite surface [20]. Raw bentonite looks more dominated by the dark than the light pattern. These results suggest an increase in pores (degree porous) after activation

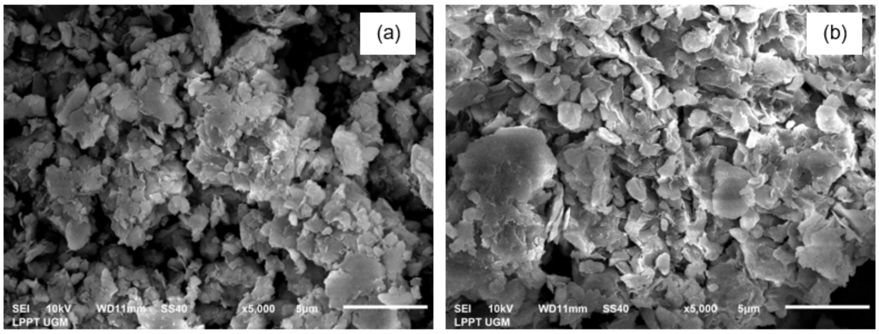

Figure 5. SEM images of (a) NB and (b) SNB-2 at 5,000× magnification.

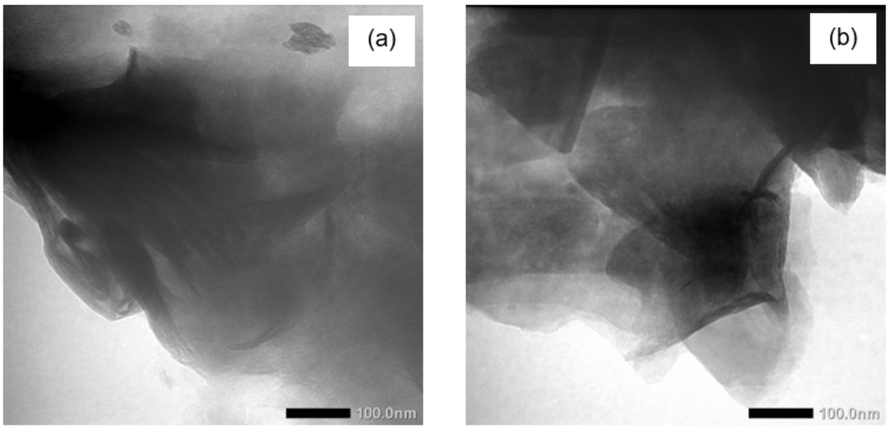

Figure 6. TEM images of (a) NB and (b) SNB-2 at 100.0 nm magnification.

with sulfuric acid [26]. Furthermore, compared to natural bentonite, the acid-activated bentonite's layered structure showed a rise in basal spacing [27].

3.1.6 Acidic properties

Fig. 7 shows the NH_3-TPD profiles of SNB-1, SNB-2, SNB-3, and SNB-4 catalysts at 100–800 °C. All materials have high desorption peaks at temperatures around 600–800 °C, which indicate strong acid sites. Low desorption peaks at temperatures around 100–300 °C indicate weak acid sites. The SNB-2 material has a low desorption peak at temperatures around 400–500 °C, which means medium acid sites. Table 3 presents the acidity value of all activated bentonite obtained from NH_3-TPD analysis. The acidity value of activated bentonite initially increased, as seen in SNB-1, to 1.58 mmol/g, and then in SNB-2, it increased to 1.72 mmol/g. However, in SNB-3 and SNB-4 samples, there was a decrease in the acidity value from 1.66 g/mol in SNB-3 to 1.44 mmol/g in SNB-4. Hence, the SNB-2 catalyst has the highest acidity value among other activated bentonite samples. This material's increasing and decreasing acidity value occurs due to the maximum ability of bentonite to adsorb ammonia in its structure. As a result, when it has reached the maximum limit of ammonia adsorption, interactions occur in its structure that will inhibit further ammonia adsorption. Therefore, the detected acidity value decreases. In addition, the increase in the Si/Al ratio will reduce the acidity value of bentonite due to the decrease in the balance of the composition in bentonite due to the loss of Al^{3+} cations. The activation process of bentonite with sulfuric acid involves changing cations from the bentonite structure, thus affecting the acidity value observed during the analysis process with NH_3-TPD [28]. The high concentration of acid used in activation can reduce the strength of the acid sites in the material.

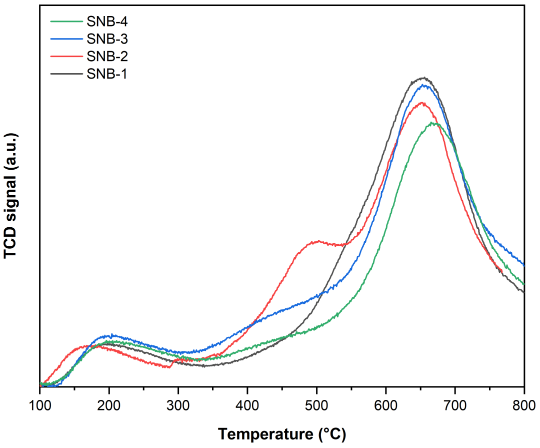

Figure 7. NH_3-TPD profiles of the catalysts.

3.2 Catalytic properties of H_2SO_4/bentonite samples

3.2.1 Effect of H_2SO_4 concentration in the catalytic properties of H_2SO_4/bentonite

The nitrobenzene synthesis involves nitric acid and benzene as the main ingredients. The benzene nitration reaction follows the electrophilic substitution reaction mechanism. The activated bentonite catalyst used in this reaction will protonate nitric acid molecules into nitronium ions, attacking the aromatic ring on the benzene compound. Nitronium ions (NO_2^+) are formed with the help of H^+ (acid sites) in the catalyst structure when mixing the catalyst with nitric acid. Then, the π electrons of the benzene aromatic will attack a nitronium ion to form the intermediate, namely the benzononium ion. Furthermore, deprotonation will occur, and nitrobenzene products will be formed [29]. The mechanism of the benzene nitration reaction can be seen in Fig. 8. The synthesis of nitrobenzene in this study was carried out using a batch microwave reactor. There are undoubtedly certain advantages to using microwave-assisted heating when applying green synthesis for a compound. One of the tenets of green chemistry is that energy requirements for chemical processes ought to be minimized because microwave heating speeds up the reaction and increases product yield while consuming less energy [30]. Compared to conventional heating, microwaves will cause a rapid temperature rise and greater heat homogeneity because they will directly

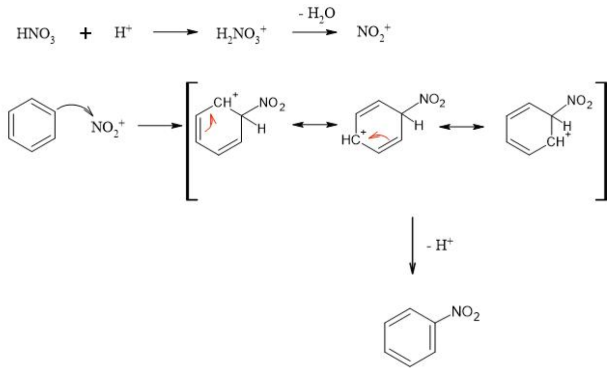

Figure 8. The mechanism of benzene nitration reaction.

Table 3. The acidity value obtained by NH_3-TPD.

Sample	Total acidity (mmol/g)	Weak acidity (mmol/g)	Medium acidity (mmol/g)	Strong acidity (mmol/g)
SNB-1	1.58	0.21	-	1.37
SNB-2	1.72	0.19	0.51	1.02
SNB-3	1.66	0.28	-	1.38
SNB-4	1.44	0.23	-	1.21

pair with polar molecules throughout the reaction mixture system [31]. Under microwave heating, reactions that take hours or days to complete under conventional heating can frequently be completed in a matter of minutes [32]. The reaction temperature is kept fixed at 60 °C to prevent the formation of by-products such as dinitrobenzene.

Catalyst performance tests were conducted using sulfuric acid-activated bentonite catalysts with a catalyst mass of 1.0 g and a HNO_3/benzene ratio of 2.63 mol/mol for 2.5 hours. Catalyst activity refers to its performance in converting benzene to nitrobenzene. In contrast, catalyst selectivity refers to the purity of nitrobenzene as the reaction product. After centrifugation, the falcon tube has three layers: the bottom is the catalyst, the middle layer is a mixture of unreacted benzene, nitric acid, and water as a reaction by-product, and the top layer is a clear yellow nitrobenzene product. As tabulated in Fig. 9, the nitrobenzene synthesis results expressed a harmonious relationship with the acidity value of sulfuric acid-activated bentonite materials. SNB-2 catalyst (2 M H_2SO_4-activated bentonite), which has the highest acidity, is able to produce the most significant amount of nitrobenzene. The higher the acidity value, the more H^+ sites are on the catalyst, so more nitronium ions are formed as the active species of the benzene nitration reaction. The GC-MS analysis results for all samples, which showed only one chromatogram peak at a retention time of about 13 minutes (Fig. 10), indicated that the synthesis product contained only one compound, nitrobenzene, and no by-products obtained from the reaction process. The stable temperature in microwave heating followed by heat homogeneity in the reaction system makes the benzene nitration reaction run well with maximum nitrobenzene product selectivity.

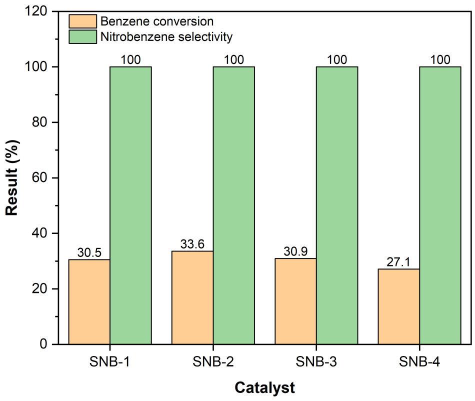

Figure 9. Benzene conversion and nitrobenzene selectivity results over sulfated natural bentonite catalysts.

3.2.2 Reusability test of the best H_2SO_4/bentonite catalyst

The reusability test was conducted by reusing the acetone-washed SNB-2 catalyst for three reaction cycles after previous use. The reusability test results of the SNB-2 catalyst with the same reaction conditions are shown in Fig. 11. In the first use (fresh catalyst), the SNB-2 catalyst produced 33.6% nitrobenzene with 100% selectivity. In the second and third uses, the catalyst still has a promising performance with a not-too-significant decrease in benzene conversion, with selectivity still at 100%. This result indicates that the activated natural bentonite catalyst has good performance stability as a solid acid catalyst in synthesizing nitrobenzene. The bentonite layer structure, which initially contained impurity ions, has been replaced by H^+ ions from sulfuric acid and formed Lewis acid sites so that the acidity and catalytic properties possessed by the SNB-2 catalyst tend to be stable. Although the percentage of the product obtained is relatively low, this result proves that sulfuric acid-activated bentonite can catalyze the nitrobenzene synthesis reaction as an alternative to replace sulfuric acid catalysts. Some previous research has successfully synthesized nitrobenzene in a batch microwave reactor using a solid acid catalyst with nitrobenzene yield and selectivity results summarized in Table 4. A sulfuric acid-activated bentonite catalyst has good potential for nitrobenzene synthesis. However, further research is needed to optimize the nitrobenzene yield and selectivity, such as examining the catalyst-to-feed ratio, reaction temperature, and reaction time. Utilizing these solid acid catalysts as a substitute for sulfuric acid homogeneous catalysts and using microwave heating assistance makes the nitrobenzene reaction safer and greener, which is certainly in line with sustainable development goals. The future is expected to create a green chemical industry.

Table 4. Comparison of previous studies in nitrobenzene synthesis using batch microwave reactor and solid acid catalyst.

Catalyst	Experimental conditions	Results	Ref.
H_2SO_4/SiO_2	T=60 °C, t=5 h, HNO_3/benzene ratio=5.96 mol/mol, m catalyst=1 g	Benzene conversion=40.3%, nitrobenzene selectivity = 100%	[18]
Sulfated natural zeolite	T=60 °C, t=2.5 h, HNO_3/benzene ratio=2.63 mol/mol, m catalyst=1 g	Benzene conversion=58.9%, nitrobenzene selectivity=100%	[19]
Sulfuric acid-activated bentonite	T=60 °C, t=2.5 h, HNO_3/benzene ratio=2.63 mol/mol, m catalyst=1 g	Benzene conversion=33.6%, nitrobenzene selectivity=100%	This study

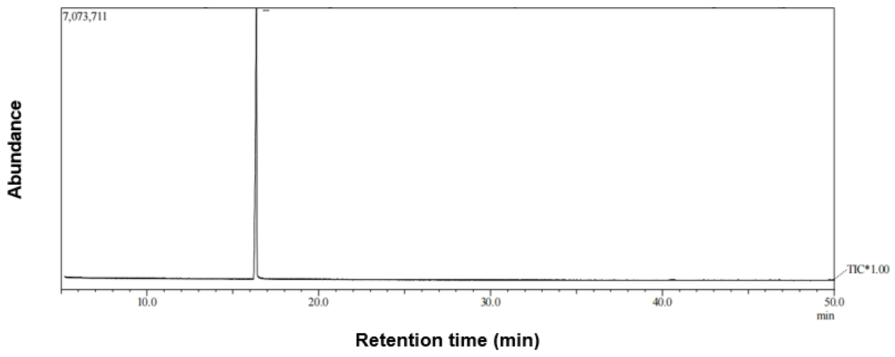

Figure 10. GC chromatogram of the reaction product.

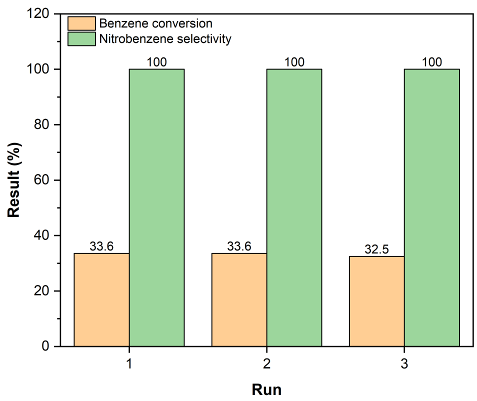

Figure 11. Reusability test results of the SNB-2 catalyst.

4. Conclusion

The effect of sulfuric acid activation with varying concentrations on the physicochemical properties of natural bentonite has been studied. Activation process with sulfuric acid increases natural bentonite's Si/Al ratio, surface area, and pore volume. Sulfuric acid treatment to bentonite material with a concentration of 2 M produces an SNB-2 catalyst, which owns the best acidity value of 1.72 mmol/g. The synthesis of nitrobenzene was successfully carried out using a batch microwave reactor at 60 °C using the SNB-2 catalyst for three consecutive runs. The benzene conversion obtained using an SNB-2 catalyst was 33.6% with a selectivity of 100%. Sulfuric acid-activated natural bentonite has the potential as a solid acid catalyst for greener nitrobenzene synthesis because it has good stability in three reaction cycles without a significant decrease in nitrobenzene yield.

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Authors Contributions
Authors were equally contributed in acquisition and analysing the data as well as preparing the paper.

Availability of Data and Materials
Data is available on request from the corresponding author, upon reasonable request.

Conflict of Interests
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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