Innovative Catalyst: Converting Methane to Methanol with Zeolite-Based ZSM-5 from Rice Husk Ash

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Abstract: Zeolite Socony Mobile-5 (ZSM-5) is a catalyst commonly used for the partial oxidation of methane to methanol. Traditionally, ZSM-5 is produced using costly and environmentally harmful organic templates. This study aimed to develop a more cost-effective and environmentally friendly method for synthesizing ZSM-5 catalysts without templates. The catalyst was synthesized from natural zeolite and rice husk ash without a template by adding ZSM-5 seeds via a hydrothermal process. The crystallization times during the hydrothermal process were 24, 72, and 144 h. X-ray diffraction (XRD) analysis confirmed the presence of a distinct peak for the synthesized ZSM-5 catalyst, indicating a successful synthesis. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) characterization revealed a hexagonal structure and a Si/Al ratio of 15.963, typical of ZSM-5. Surface area analysis (SAA) showed that the surface areas of the ZSM-5 catalysts were 47.667 m²/g after 24 h, 71.158 m²/g after 72 h, and 74.760 m²/g after 144 h, indicating that longer crystallization times resulted in a larger surface area. In methanol production tests, the ZSM-5(24 h), ZSM-5(72 h), and ZSM-5(144 h) catalysts achieved methanol concentrations of 9.05%, 10.34%, and 18.15%, respectively. These results suggest that crystallization time significantly affects both the surface area and catalytic performance of ZSM-5.
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Keywords: methane conversion; nature based-ZSM-5; non-template; zeolite

1. Introduction

Rising greenhouse gas emissions from human activities contribute significantly to global warming and climate change[1]. Indonesia has set a goal to attain net-zero emissions by 2060 by implementing strategies to reduce overall emissions. Investigating green technologies is critical for reducing emissions and for generating green energy[2]. Methane, a potent greenhouse gas with a global warming potential 21 times higher than that of carbon dioxide, exacerbates pollution[3]. As human activities intensify, methane emissions increase, potentially surpassing natural methane emissions. An effective strategy for mitigating methane pollution is to convert it into methanol[4]. Methanol, a versatile hydrocarbon, is utilized in various applications, including fuel, preservatives, and coating materials such as formaldehyde, adhesives, and food components.

Methanol can be generated from methane via two primary processes: steam reforming and partial oxidation. Steam reforming consisted of two stages. First, methane is transformed into synthesis gas (syngas) at temperatures ranging from 500 °C to 1100 °C and pressures between 15 and 30 atm using a nickel catalyst. In the second stage, syngas, which comprises CO_2 and H_2, is converted into methanol using a copper-zinc/alumina catalyst, with pressures between 50 and 100 atm and temperatures between 220 and 300 °C[1,5]. Although steam reforming is effective, it is not environmentally friendly because it releases substantial amounts of greenhouse gases into the atmosphere.

The steam reforming process requires substantial energy owing to the stability of the symmetric C-H bond in the methane[6]. In response, researchers have turned to partial oxidation as an alternative method to produce methanol. However, partial methane oxidation has not yet

resulted in significant methanol yields[4]. To address this issue, an innovative approach involves the use of dual-function catalysts, one for high-temperature reactions and another for low-temperature reactions. The energy required to break the strong carbon-hydrogen bond in methane into hydrogen and methyl radicals is 439 kJ/mol[7]. To increase methanol production, catalysts must prevent simultaneous methanol oxidation and focus solely on activating the methane[1]. Therefore, the selection of an appropriate catalyst is essential for achieving high methanol productivity.

The production of methanol from methane using catalysts has been widely examined. Among the various catalysts studied, ZSM-5 (Zeolite Socony Mobile-5) has received the most attention. ZSM-5 is a crystalline, porous aluminosilicate with varying channel and void sizes, accommodating different molecules[8-10]. This zeolite is utilized in several chemical reactions, including alcohol dehydration and alkane cracking, in which hierarchical ZSM-5 (HZSM-5) catalyzes these reactions[11]. ZSM-5 catalysts can be synthesized using both natural and synthetic materials. Natural materials are preferred because of their high cost and environmental impact of chemicals[12]. Yanti et al.[13] combined fly ash from coal and rice husks to create zeolite ZSM-5. Two different templates, tetrapropylammonium hydroxide (TPAOH) and polydiallyldimethyl ammonium chloride (PDDA), were employed in the hydrothermal treatment process to create a ZSM-5 catalyst. The results demonstrated that the ZSM-5 catalyst derived from biomass waste can be utilized as a catalyst for partial oxidation to produce methanol from methane.

Metta et al.[14] examined the application of rice husk ash and coal fly ash waste in the synthesis of ZSM-5 catalysts. This research focused on the importance of the Si/Al ratio, which is a critical factor in catalyst production. ZSM-5 catalysts were prepared in an autoclave at 180 °C using Si/Al ratios of 20, 30, 40, 50, and 60 mol/mol. The results demonstrate that ZSM-5 catalysts were formed at all Si/Al ratios. The catalyst synthesized at a 50 mol/mol ratio exhibited a crystallinity of 52.83 %. However, the products exhibited negative effects, including the presence of silica oxide and analcime. In addition to coal fly ash, natural zeolite is a promising source of silica and alumina for ZSM-5 synthesis. Indonesia, situated between multiple volcanic belts and oceans, has a significant potential for natural zeolite mineral deposits[15,16].

The crystals of the ZSM-5 catalyst that were produced exhibited a hexagonal form. Achieving a phase-pure ZSM-5 catalyst with a Si/Al ratio of less than 15 is particularly challenging when employing the commonly used tetrapropyl ammonium (TPA) template[17-19]. In contrast, Yanti et al.[20] successfully synthesized ZSM-5 catalysts from coal fly ash and rice husk ash using a nontemplate method. This method demonstrated that it can be to synthesize ZSM-5 without a template. Lestari et al.[21] successfully synthesized ZSM-5 via a seeding technique in which silica was derived from rice husk, alumina, and silica from coal bottom ash. The synthesis was conducted using a commercial ZSM-5 catalyst as the seed and a hydrothermal technique in an autogenous autoclave for 36 h at 180 °C. The ZSM-5 seed acted as a structure-directing agent, and modifications to the catalyst structure enhanced its porosity[22]. Previous studies have shown that ZSM-5 catalysts can be effectively produced from natural materials using ZSM-5 seeds instead of a template to achieve high crystallinity. Utilizing coal fly ash (CFA) and bottom ash (BA) as sources of silica and alumina typically requires pre-treatment, such as acid treatment, to eliminate impurities that may have environmental impacts[23]. Conversely, the natural zeolite used in this study served as a source of alumina and silica, without requiring purification. This advantage can be attributed to its composition, which consists mainly of alumina and silica.

The objective of this study was to explore the synthesis of ZSM-5 catalysts using natural zeolite (NZ) and rice husk ash (RHA) as the primary sources of alumina and silica, respectively. This study employed a non-template methodology and manipulated the hydrothermal crystallization duration to produce ZSM-5 catalysts with high degrees of crystallinity. Subsequently, the ability of the synthesized catalysts to convert methane into methanol was evaluated. This research endeavors to establish an eco-friendly and economically viable approach for catalyst production by utilizing naturally occurring materials, thereby potentially contributing to sustainable advancements in chemical synthesis.

2. Material and methods

2.1 Materials

The ZSM-5 catalyst was produced using natural zeolite from Sukabumi, West Java, Indonesia and rice husk ash from Bogor, West Java, Indonesia. Additionally, hydrochloric acid (HCl, 37%) from Smart Lab, sodium hydroxide (NaOH) from Merck, and glacial acetic acid from Smart Lab were used. Distilled water from the Energy and Chemical Industry Laboratory (BRIN) was used, along with a commercial ZSM-5 catalyst P-26 variant (ACS Material) as a reference material for catalytic activity testing, and 100% Supelco ethanol was employed as the solvent.

2.2 Preparation of the catalyst

2.2.1 Raw material preparation for ZSM-5 synthesis

The process of refining rice husks involves the removal of impurities, meticulous cleaning, and subsequent grinding of the material into a fine powder. Subsequently, this powder was subjected to a four-hour burn at 700 °C in a furnace, resulting in the production of rice husk ash. Next, natural zeolite was carefully selected and filtered through a 200-mesh screen. Subsequently, the zeolite was heated for three hours at 500 °C in a furnace, which

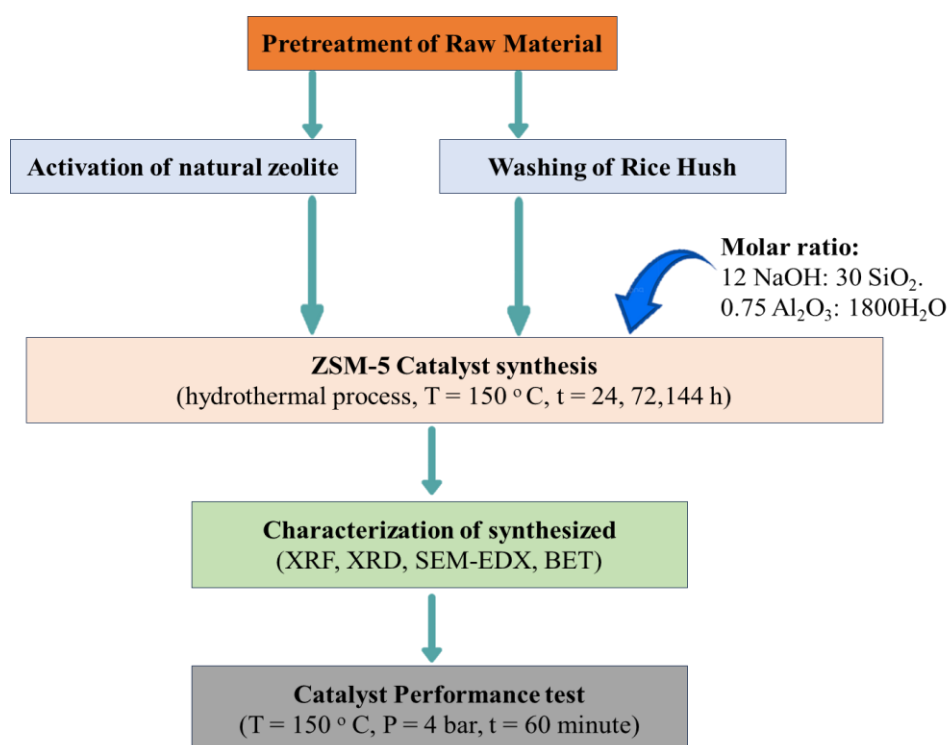activated it and yielded natural zeolite material.

Fig. 1: Scheme of Synthesizing ZSM-5 Catalyst.

Subsequently, a one-molar solution of hydrochloric acid was introduced to the activated natural zeolite, which was agitated for a period of three hours at a temperature of 90 °C to attain purity. The sample was then filtered and dried overnight before being thoroughly cleaned with distilled water until the pH reached a state of neutrality. The crystalline compositions of rice husk ash and natural zeolite were analyzed using X-ray fluorescence (XRF).

2.2.2 ZSM-5 synthesis

ZSM-5 catalysts were synthesized using natural zeolite as a source of alumina and silica and rice husk ash as an additional source of silica, a molar ratio of 12 NaOH, 30 SiO_2, 0.75 Al_2O_3, and 1800 H_2O as shown in Fig. 1. The process commenced from the preparation of Mixture A involved mixing 30 mL of 0.4 N NaOH with natural zeolite and agitating it for 2 h at 100 °C. Similarly, Mixture B was prepared by combining rice husk ash with 70 mL (0.4 N NaOH and agitating it under the same conditions. Mixtures A and B were then combined and stirred continuously for one hour at 100 °C. Subsequently, the mixture was stirred for 2 h at 100 °C in a 2.5% ZSM-5 catalyst seed. Glacial acetic acid solution was added to adjust the pH to approximately 11, and the mixture was agitated at 100 °C for 3 h. The blend was stirred at ambient temperature for an entire day. Finally, the crystallization was carried out in a Teflon autoclave at 150 °C, with varying durations of 24, 72, and 144 h.

2.3 Characterization of synthesized ZSM-5 Catalyst

The material structure was examined using X-ray diffraction (XRD, SMARTLAB RIGAKU). The morphology of the material was investigated using Jeol JSM-IT200 Scanning Electron Microscopy, while the Quantachrome Novatouch LX 2 was utilized to characterize the surface area and pores of the synthesized ZSM-5 catalyst.

2.4 Catalytic Performance Test

A partial oxidation method with ratio methane and oxygen are 1 and 0.5 was used to convert the methane into methanol. The reaction was carried out in a 500 mL batch reactor using ultra-high-purity (UHP) methane gas at an initial pressure of 4 bar and a temperature of 150°C for one hour. This study compared the results of the reaction using a commercial ZSM-5 catalyst and a synthesized ZSM-5 catalyst, each weighing 1 g, with a reaction conducted without a catalyst. Ten milliliters of pure ethanol was used as solvent for each reaction.

Product analysis was carried out using gas chromatography with flame ionization detection (GC-FID) for both the gas and liquid phases. The following conditions were used for the analysis: the injector was set at 150 °C, the detector was set at 200 °C, and the column temperature was initially set at 40 °C for a period of five minutes. The temperature was then increased at 5 °C/min until it reached 170 °C, which was maintained for ten minutes. The methanol concentration was determined by interpolating the methanol peak area from the

chromatogram of the product against a methanol standard curve.

3. Result and discussion

3.1 Chemical component analysis

Rice husk ash (RHA) and natural zeolite (NZ) were analyzed using X-ray fluorescence (XRF) to identify their chemical components. The primary objective of this characterization was to determine the concentrations of silicon (Si) and aluminum (Al) in both RHA and NZ. The XRF analysis results for the RHA and NZ are presented in Table 1.

Table 1. Result of RHA and NZ's XRF characterization.

Chemical Composition of RHA	Kadar (%w/w)	Chemical Composition of NZ	Concentration (%w/w)
Si	85.052	Al	44.066
Al	12.819	Si	40.980
Fe	0.047	Ca	7.765
V	2.039	K	4.658
Mn	0.012	Fe	2.335
Yb	0.012	Mn	0.052
Rh	0.006	Sr	0.118
Os	0.002	Cu	0.003
Ni	0.001	Pb	0.002

According to Table 1, the analysis of rice husk ash (RHA) indicates that it comprises 85.05% w/w silica, an amount that aligns with other studies conducted using the same rice husk source and reporting an 85% silica concentration in the ash[21]. Additionally, the table reveals the presence of several metals such as Sr, Pb, Zn, Ca, and K, which function as surface cations in zeolite minerals[24]. Natural zeolite (NZ) primarily consists of alumina (Al_2O_3) and silica (SiO_2), along with various other organic and inorganic components. To improve the porosity and surface area of NZ, acid is used to dissolve the remaining metal oxides[25].

3.2 Structure analysis

X-ray diffraction (XRD) is an essential method for analyzing the atomic structure of crystalline solids. In this study, the XRD pattern of the synthesized ZSM-5 catalyst was compared to the reference diffractogram from the International Zeolite Association (IZA) database to confirm the ZSM-5 framework. The XRD characterization was aimed at validating the formation of ZSM-5 from the completed synthesis process. Among the samples, ZSM5-144 demonstrated the highest catalytic activity and was selected for further characterization. Figure 2 shows the XRD diffractogram pattern of the ZSM5-144 sample.

X-ray diffraction (XRD) analysis of the ZSM-5 catalyst pattern exhibited intense diffraction peaks at 2θ locations of 7-9° and 22-25°, which align with the characteristic peaks of standard ZSM-5 (IZA) data[26]. This finding confirms the formation of the Mordenite Framework Inverted (MFI) structure, as indicated by the Joint Committee on Powder Diffraction Standards (JCPDS) 44-000326-28[27-29]. XRD characterization of the synthesized catalyst sample revealed a typical peak of ZSM-5 with an MFI structure, as evidenced by the diffraction peaks at 2θ = 7.9°, 8.8°, 23.1°, 23.3°, 23.9°, and 24.4°. Analysis also indicated that the ZSM-5 catalyst had a crystallinity of 94%. Figure 2 displays a typical analcime peak at 2θ = 15.9° and 26.1° with high peak intensities.
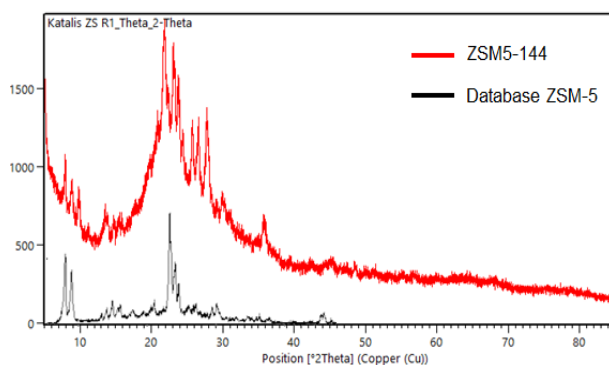

Fig. 2: XRD pattern of XRD pattern of as-synthesized ZSM-5.

3.3 Material morphology

Scanning electron microscopy (SEM) was used to investigate the morphological structures of the commercial and synthesized ZSM-5 catalysts. The SEM operates by scanning the surface of a sample with a focused beam of electrons, resulting in the production of images[30]. The results of the analysis are shown in Fig. 3. Additionally, energy-dispersive X-ray (EDX) analysis was performed to determine the chemical compounds present in the samples. Figure 3(a) and 3(b) illustrate the crystal morphologies of commercially available and synthesized ZSM-5 catalysts, respectively. Figure 3(c) shows the elemental distribution within the synthesized ZSM-5 catalyst structure.

Figure 3(a) and 3(b) show a coffin-shaped (hexagonal) morphology, which is consistent with the shape observed for both the synthesized and commercial ZSM-5 catalysts. According to Yaripour et al.[31], ZSM-5 has a hexagonal crystal shape because of the hydrothermal process. The shape of the ZSM-5 catalyst was hexagonal, with an estimated length of 8.4 - 9.5 μm and a width of 6.2 - 7.5 μm, as shown by the hexagonal structure in Fig. 3(a). The surface of the ZSM-5 catalyst remained asymmetrical because a significant number of particles continued to adhere to each other, forming clumps. These clumps suggest that the synthesized ZSM-5's particle shape is irregular and inconsistent, which lowered the crystallinity. This irregularity results from the ZSM-5 catalyst synthesis method using natural materials (rice husks and natural zeolite), which, despite pretreatment, has different surface structures[22]. However, several factors can influence the ZSM-5 crystal shape during zeolite synthesis, including the type of raw materials, the temperature at which

crystallization occurs, the Si/Al ratio, the duration of crystallization, and other process parameters[14]. While Si and Al were obtained via the use of natural zeolite and rice husk ash as the raw materials for zeolite creation, Fig. 3(c) depicts the distribution of Sodium (Na) in the synthesized

ZSM-5 catalyst as a result of the use of NaOH during zeolite synthesis. Effective stirring and mixing during zeolite production led to a uniform particle distribution, as evidenced by the relatively equal elemental distribution in Fig. 3(c)[20].
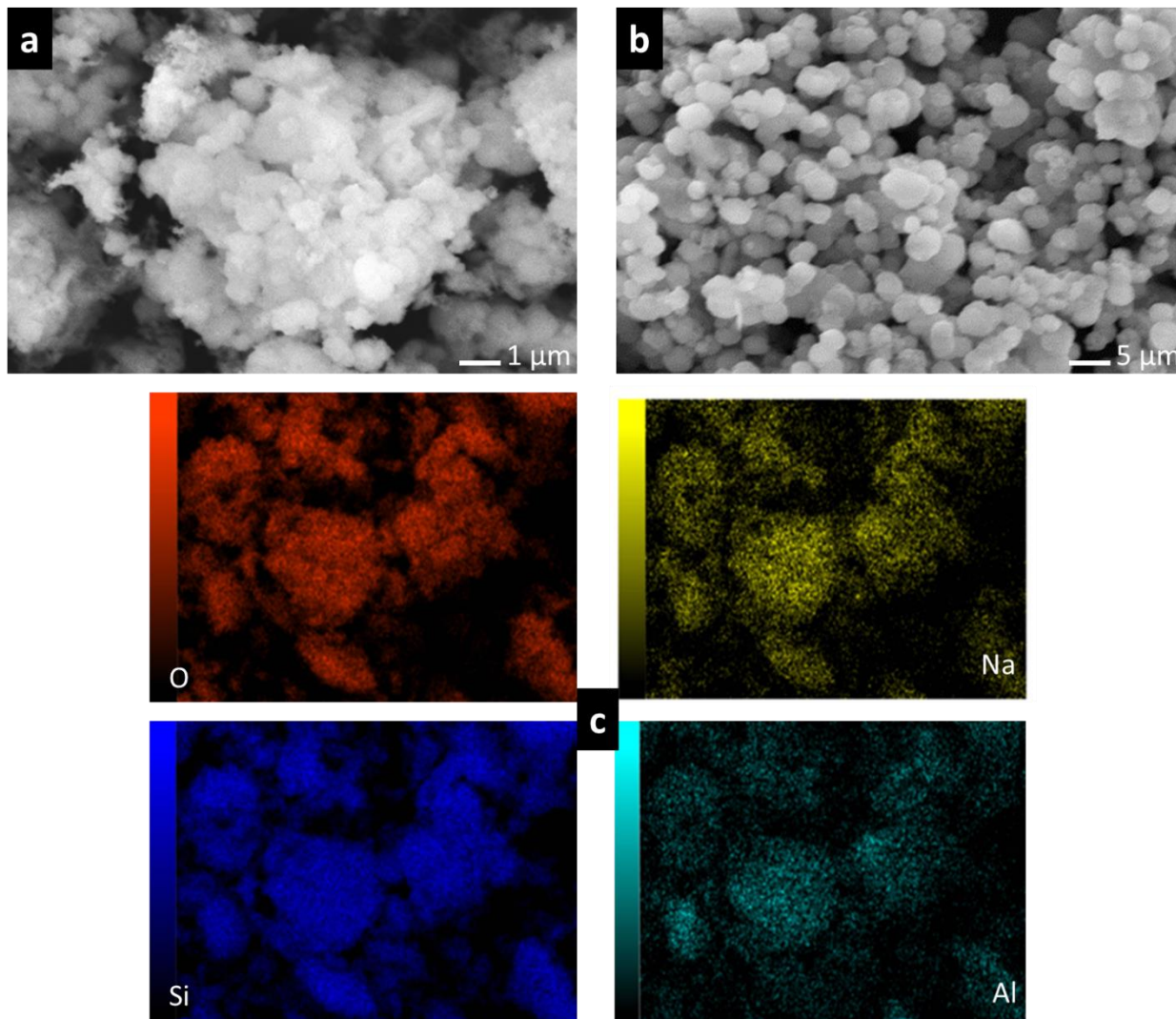

Fig. 3: SEM image of (a) ZSM-5 catalyst (b) commercial ZSM-5 catalyst, (c) element distribution of ZSM-5 catalyst.

The sample's chemical composition was analyzed using EDX, with a specific focus on the silicon (Si) to aluminum (Al) ratio, as well as other compositional characteristics. The Si/Al ratio is a crucial factor for determining the composition and catalytic properties of ZSM-5
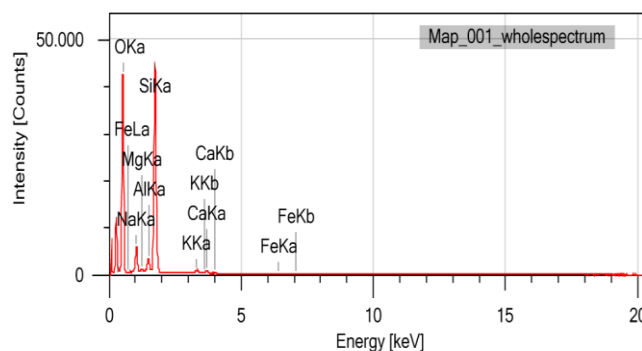

Fig. 4: EDX mapping element of synthesized ZSM-5.

Figure 4 shows the elemental composition and percentages of the as-synthesized ZSM-5 catalyst, as determined by EDX mapping. The analysis showed that

the percentages of silicon (Si) and aluminum (Al) are 30.01% and 1.88%, respectively, indicating a significant incorporation of Si during the synthesis process. EDX mapping was employed to confirm the Si/Al ratio of the as-synthesized catalyst, which was found to be 15.96. Although this ratio is lower than the calculated value based on the synthesis formula, it is consistent with the anticipated high silica concentration[32,33]. The discrepancy between the measured and calculated Si/Al ratios can be attributed to the limitations of the SEM-EDX test[30].

Although the ZSM-5 catalyst produced has a Si/Al ratio that meets the specified requirements, it contains impurities, including magnesium, potassium, calcium, and iron. The trace amounts of these impurities suggest potential contamination in the catalyst, which may have originated from the raw materials used during the pretreatment process[34,35].

3.4 Surface area analysis

The duration of the crystallization process (t) was altered for the ZSM-5 catalysts, encompassing periods of 24 (ZSM5-24), 72 (ZSM5-72), and 144 h (ZSM5-144), in addition to the commercial ZSM-5 catalyst. The surface areas of both the commercial and synthesized ZSM-5 catalysts were determined using a Quantachrome Novatouch LX2 Surface Area and Pore Size Analyzer. The results of the surface area analysis for the ZSM-5 catalysts are summarized in Table 2, and Fig. 5 illustrates the adsorption-desorption isotherm curves.

Table 2. Result of BET Analyzer.

Catalyst	Specific surface area (m^2/g)	Total pore volume (cm^3/g)	Mean pore diameter (nm)
ZSM5-24	47.667	1.0677	4.4798
ZSM5-72	71.158	0.0739	2.0079
ZSM5-144	74.760	0.0775	2.0745
ZSM-5 Com	36.178	0.2405	3.2462

The results of the surface area analyses of the ZSM-5 catalysts, presented in Table 2, indicate that the ZSM-5 catalysts synthesized from natural zeolite and rice husk ash possess a smaller surface area than the commercial ZSM-5 catalyst. This reduction in the surface area can be attributed to the presence of impurities, which may hinder the zeolitization process[34]. As shown in Table 2, prolonging the crystallization duration led to an increase in the total surface area of the catalyst. Specifically, the surface area increased from 47.667 m^2/g for ZSM5-24 to 71.158 m^2/g for ZSM5-72, and further to 74.760 m^2/g for ZSM5-144. This trend aligns with the findings of Krisnandi et al. and suggests that extending the crystallization time enhances both nucleation and growth rates, resulting in a general increase in crystallinity[33].

The International Union of Pure and Applied Chemistry (IUPAC) categorizes porous materials into three categories based on their pore diameters: microporous (0.3 2 nm), mesoporous (2–50 nm), and macroporous (> 50 nm)[36]. As indicated in Table 2, all the ZSM-5 catalysts, whether commercial or synthesized, fall under the mesoporous classification. Pore size plays a crucial role in determining the surface area and adsorbent capacity, particularly in gas-phase adsorption applications. Mesoporous materials are well suited for gas-phase processes as they offer a larger overall surface area owing to the decrease in pore size[37].

The synthesized ZSM-5 catalyst exhibited a notable pore distribution within the 2–5 nm range, as evidenced by the Barrett–Joyner–Halenda model. The efficiency of the catalyst depends on the accessibility of the reactants within the pores during the catalytic activity test[14]. The pore size distribution data revealed inconsistencies across the samples, which could be attributed to the various pore distributions arising from the amorphous phases present in the samples. Employing natural materials as the primary ingredients for catalyst synthesis may contribute to the disparity in pore size distribution[20].

The synthesized ZSM-5 catalyst is categorized as having a type IV isotherm, which involves adsorption from mesoporous materials with pore sizes ranging from 2 to 50 nm. This type of isotherm is characterized by the presence of hysteresis loops, as demonstrated by the adsorption-desorption isotherm curves depicted in Fig. 5. According to Metta et al.[14], a hysteresis loop occurs when the amount of desorbed gas differs from the amount initially adsorbed during the gas desorption process, particularly when the pressure is decreased. This phenomenon suggests that the inner and outer pores of the mesoporous materials have different sizes. The inner pore size is larger than the outer pore size, which results in a slower desorption process than the adsorption process owing to the presence of residual nitrogen gas in the cave-shaped pores[38]. The amount of gas remaining on the pore surface of the material during desorption was still higher than that adsorbed at the same pressure. This indicates that more nitrogen gas was desorbed than absorbed. As shown in the isotherm curve images, there was minimal gas adsorption at a pressure of P/Po = 0.1. However, an increase in pressure from P/Po = 0.1 to 0.3 suggests that the mesoporous material is filling up during this range.

3.5 Catalytic Performance Test

A stainless steel batch reactor was used to evaluate the catalytic efficiency of methane conversion to methanol. Prior to the catalytic reaction, the synthesized ZSM-5 catalyst underwent a three-hour calcination process, which was crucial for activating and purifying the catalyst pores by removing contaminants and water vapor[33]. Nitrogen gas was used to remove organic contaminants, water vapor, and excess oxygen from the reactor. The reaction conditions were set at an initial CH_4 pressure of 4 bar, a temperature of 423 K, and a reaction time of 60 min. The results of this performance test are shown in Fig. 6.
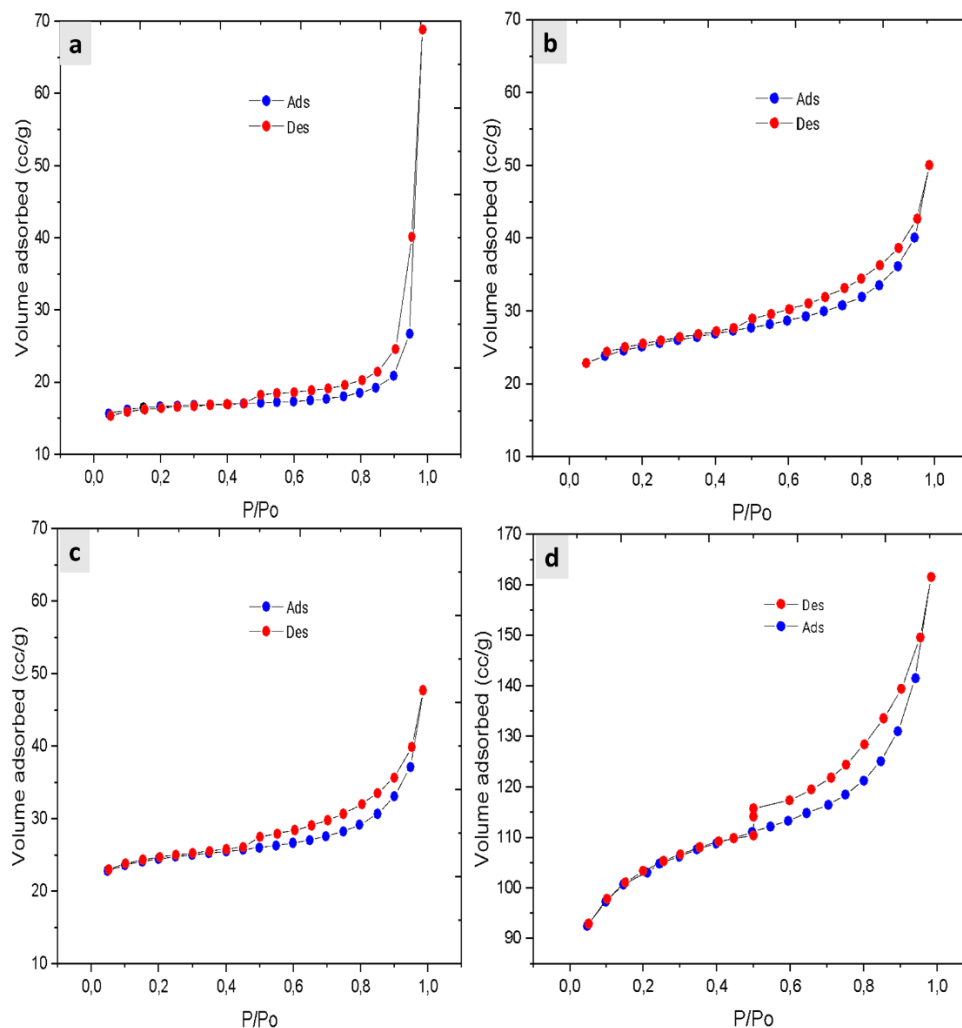
Fig. 5: The isotherm adsorption-desorption curves of (a) ZSM5-24 (b) ZSM5-72 (c) ZSM5-144 (d) ZSM-5 Com.

The data presented in Fig. 6 demonstrate that both the commercial ZSM-5 catalyst and the non-catalytic reaction resulted in lower methanol conversion rates compared to the synthesized ZSM-5 catalysts. This difference in the conversion rates is attributed to the presence of metal oxide species such as Fe, Mg, Na, and Ca on the surface of the zeolite[20,21]. Additionally, the reaction conditions played a significant role in the methanol yield. As depicted in Fig. 6, under the same reaction time of 60 min, the catalyst resulted in higher methanol concentrations than in the non-catalytic reaction. Among the synthesized ZSM-5 catalysts, those with longer crystallization times showed higher methanol concentrations of 9.05%, 10.34%, and 18.15% after 24, 72, and 144 h of crystallization, respectively. This trend is consistent with the surface area analysis results, which indicate that the surface area of the catalyst increased with longer crystallization times. Therefore, the increased surface area of the catalyst directly correlates with enhanced performance and higher methanol yields[33].
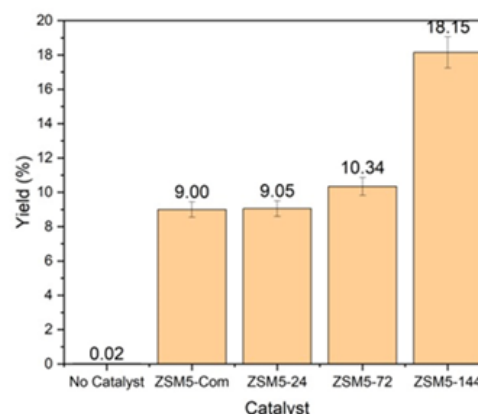

Fig. 6: The yield of methanol with catalyst variable.

Figure 7 demonstrates that the ZSM-5 catalyst, following calcination (MO+ZSM-5), effectively decomposed hydrogen atoms from strong C-H bonds. During calcination, the ZSM-5 catalyst generated an O (oxo) species. The methanol synthesis mechanism from partial methane oxidation, depicted in Fig. 7, involves two transition states, resulting in methanol formation with a lower activation energy[39]. This section describes the

procedure employed to explain the partial oxidation reaction that converts methane into methanol, which consists of C-H activation, hydroxy formation, methanol formation, and methanol desorption[13].
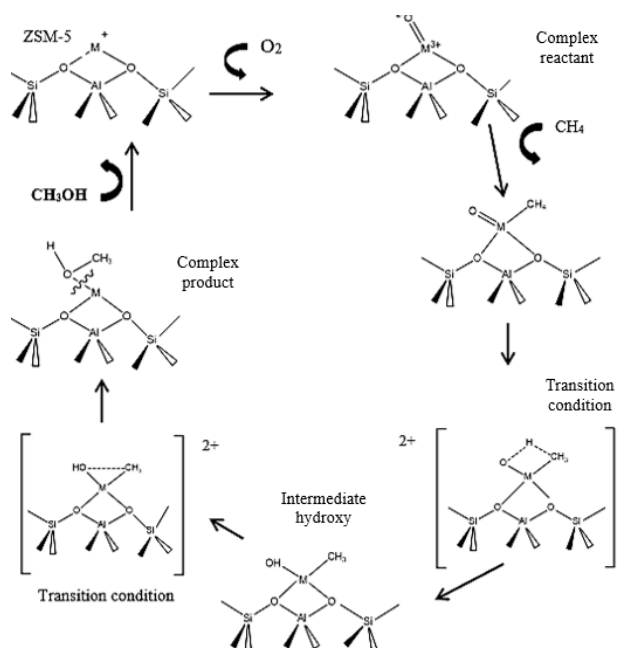

Fig. 7: Mechanism of ZSM-5-mediated partial oxidation process that produces methanol.

4. Conclusion

The production of ZSM-5 catalysts from natural zeolite and ash from rice husks without the use of a template has been confirmed through various characterization techniques, including X-ray diffraction, scanning electron microscopy with EDX, and surface area analysis. The XRD data revealed that ZSM-5 exhibited characteristic peaks at $2\theta = 7.9°$, $8.8°$, $23.1°$, $23.3°$, $23.9°$, and $24.4°$, which suggested the formation of a hexagonal structure with a Si/Al ratio of 15.96. Furthermore, the SEM-EDX results corroborate this, indicating surface areas of 47.667, 71.158, and 74.760 m²/g for the ZSM5-24, ZSM5-72, and ZSM5-144 catalysts, respectively.

In the partial oxidation process, the concentration of methanol without the aid of a catalyst was 0.02 percent. The utilization of the ZSM-5 catalysts led to a significant increase in methanol production. The highest concentration of 18.15 percent was achieved using ZSM5-144, followed by 10.34 percent for ZSM5-72, and 9.05 percent for ZSM5-24. Future research should focus on investigating alternative natural materials that can serve as silica sources for the synthesis of ZSM-5. Moreover, incorporating active metals such as Cu, Fe, and Co into the ZSM-5 catalyst may enhance its performance and selectivity.

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