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Impregnation Effect of Iron (Fe) and Cobalt (Co) on ZSM-5 Zeolite Catalyst from Rice Husk Ash and Coal Fly Ash for Methanol Synthesis

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Abstract: The methanol production process is a major issue due to the importance of methanol applications in transportation and other chemical industries. Selective catalysis of methane to methanol conversion using specific catalysts is one of numerous efficient methanol production processes now being developed by researchers worldwide. In the current study, we investigated the effectiveness of ZSM-5 zeolite-supported iron oxide and cobalt oxide as catalytic agents. The ZSM-5 zeolite employed (synthesized ZSM-5) was developed through a non-template approach by using ash from rice husk (RHA) and fly ash from coal (CFA). Wet impregnation method was used to impregnate the synthesized ZSM-5 with iron (Fe) and cobalt (Co), and a commercial ZSM-5 was likewise impregnated with Fe and Co for comparison. XRD, BET, and SEM-EDX ware used to examine the zeolite structure of the synthesized ZSM-5, and results discovered that the zeolite had been successfully created from rice husk ash and coal fly ash. The synthesized ZSM-5 samples were tested in a batch reactor for an hour at 423 K and 4 bars of initial methane pressure to accomplish methane to methanol conversion in an effort to quantify the catalytic activity. The results revealed that Fe impregnation of synthesized ZSM-5 zeolite had a greater effect on increasing methanol yield than Co impregnation.

The catalytic performance test was impacted by Fe and Co impregnation in ZSM-5. This shows that the methanol yield of the synthesized ZSM-5 can be increased by Fe impregnation to 13.12% from 10.04% without it.

Keywords: zeolite catalyst; coal fly ash; rice husk ash; impregnation; methanol

1. Introduction

Methane is an important fuel and feedstock that plays a critical role in meeting the world's energy needs. However, when burned, methane has a 28-times greater potential than carbon dioxide to cause global warming, making it a harmful greenhouse gas.[1)]. To meet the global target of GHG emission reduction in the energy sector, the increasing use of methane as an attractive feedstock that can be converted into a highly desirable chemical has become the most challenging thing over several decades[2)]. Due to its stability, ease of transportation, capacity to be converted into the green fuel hydrogen, and extensive use in both the chemical and transportation industries, the process of converting methane into methanol has been receiving a lot of interest. Currently, methane to methanol conversion on an industrial scale develops by indirect route-steam reforming of natural gas, which is later used in methanol synthesis[2)]. This indirect methanol synthesis involves a high-energy-intensive that includes the syngas conversion stage. More energy-efficient direct conversion methanol derived from methane would be considerable although this approach is still limited by its low selectivity[3]. The key challenges associated with the selective methane to methanol conversion are closely related to the catalyst performance. The performance of catalyst can be improved by adding selective metals containing an oxidation number of more than +2 that interacted with methane to create C1-oxygenate such as methanol[4].

The catalyst zeolite ZSM-5 is widely used in the petroleum cracking reaction due to its uniform pore size, large surface area, and acidic properties[5]. Various studies on improved modified zeolite catalysts have been carried out through ion-exchanged with different metals. Copper-exchanged ZSM-5 is the most studied, Cu-ZSM-5 was conducted by Woertink et al[6]. However, the acetonitrile/water mixture used for the methanol extraction and the activation of oxygen at a higher temperature (723K) made the method undesirable. Another study reported the influence of cobalt insertion on the hierarchical ZSM-5 using the ion exchange method carried out by Krisnandi et al[7]. However, the methane conversion still remains low at 7.56% due to the amount of cobalt oxides present as an active catalyst was insufficient to balance the negative formal charge of ZSM-5.

Moreover, Krisnandi et al[8] reported Co-oxide modified ZSM-5 were prepared through wet impregnation method. Incipient wet impregnation is the most common way of introducing selective metals to catalysts, particularly on mesoporous supports (pore width 2-50 nm). The result show that a more active cobalt compound on Co/ZSM-5 catalyst has the ability to enhance methanol yield reaches 42.56%. Further research looked into alternatives to cobalt oxide to alter NaY zeolite, including Mn_3O_4, NiO, Fe_2O_3, and Fe_3O_4[9]. The investigation came to the intriguing conclusion that the iron oxide species is greatest candidate for producing a higher yield of methanol up to 30%. Furthermore, iron is better suited for syngas conversion with a lower H_2/CO ratio produced from biomass or coal[10]. However, the material sources for ZSM-5 catalyst usually are pro-analysis grade materials, which are expensive.

Yanti et al[11] conducted the successful synthesis of ZSM-5 catalysts from coal fly ash (CFA) and rice husk ash (RHA) using two different type of templates (TPAOH and PDDA). Attempt to improve catalyst performance by metal insertion on zeolite catalyst has not included in this study. In addition, using organic templates as an zeolite framework formation is more expensive, impacts the risk of environmental pollution, and causes irreversible lumps on the crystal that change the Si/Al ratio[12].

Therefore, this study will assess the synthesis of nature-based ZSM-5 from CFA and RHA using a non-template method. The synthesized ZSM-5 zeolite was impregnated with iron (Fe) and cobalt (Co) at varied concentrations for the purpose to examined the reaction toward methanol. In addition, to better understand how these metals affect the methane to methanol, impregnation of commercial ZSM-5 by cobalt and iron was also examined.

2. Material and methods

2.1 Materials

ZSM-5 zeolite production are fly ash from coal (CFA) as silica and alumina source from Paiton Coal Power Plant Unit 5&6 (PT. Jawa Power), ash from rice husk (RHA) as silica source from Bogor, West Java, Chloride Acid (HCl) 37% and Natrium hydroxide (NaOH) from Supelco, Glacial Ethanoic Acid 99,7% from Smart Lab, $Co(NO_3).6H_2O$ and $Fe(NO_3)_3.9H_2O$ from Merck and distilled water. Materials used for catalytic activity testing are commercial ZSM-5 P-26 type (ACS Material) as a comparison and absolute ethanol from Supelco as a catalyst solvent.

2.2 Catalyst preparation

Preparation of raw material for ZSM-5 production

Fly ash from coal that has been selected and screened through a 200 mesh sieve was activated by heating it for two hours in a furnace at 800°C. The activated CFA was then purified for three hours at 90°C by adding a 1 molar HCl solution. Thereafter, sample was filtered, air-dried, and finally rinsed with distilled water to ensure that the pH level was neutral. For producing ash from rice husk material, the rice husk was cleaned to eliminate its contaminants then washed and mashed before being processed into ash by burning it in a furnace at 700°C for one hour. The crystalline components of CFA and RHA were examined via X-Ray Diffraction (XRD) SMARTLAB RIGAKU.

ZSM-5 synthesis

ZSM-5 synthesized using alumina and silica sources, which derived from CFA and RHA [10] was conducted at a molar ratio 30 SiO_2: 0.75 Al_2O_3: 12 NaOH: 1800 H_2O. The first mixture of coal fly ash and 30mL NaOH 0.4N was stirred for 2 hours at 100°C (mixture A). The second mixture consists of rice husk ash and 70mL NaOH 0.4N (mixture B) was treated the same as mixture A. After that, mix the mixture of A and B while still stirring for 1 hour at 100°C. Then add ZSM-5 as seed as much as 1 % to the mixture and stir for 2 hours at 100°C. After adding a glacial acetic acid solution, the mixture's pH was likely adjusted up to 11, and stirring was maintained at 100°C for 3 hours. After that, it required 24 hours of mixing at room temperature. while being agitated. After that, the crystallization procedure was carried out in an autoclave made of teflon for 144 hours at a temperature of 150°C.

2.3 Impregnation of Fe and Co into ZSM-5

Through the use of the impregnation process, a total of 2.5%wt of the ZSM-5 catalyst was combined with a solution containing Fe (III) and Co (II). The impregnation of Fe metal and Co metal was accomplished by dissolving in distilled water. Then, gradually incorporate the Fe solution into ZSM-5 until a slurry forms. After that, a paste was formed by mixing the mixture at room temperature for a full 24 hours. After the paste formed, it was dried for one night at 60°C and then calcined for three hours at 500°C. The XRD and the BET analyzer were utilized in order to perform the process of characterizing both unimpregnated and impregnated ZSM-5.

2.4 Characterization of synthesized ZSM-5

Synthesized ZSM-5 structure was characterized with XRD SMARTLAB RIGAKU, Jeol JSM-IT200 Scanning Electron Microscopy (SEM) and Quantachrome Novatouch LX 2 Pore Size, Surface area, Pore Volume analyzer with degassing temperature 300°C for 3 hours. For SEM analysis, sample was coated by Au and analyzed using a magnification of 3000, 5000, 10000, 20000 and 30000, type image SE and BSE with high vacuum condition (10^{-2} - 10^{-3} Pa).

2.5 Catalytic Performance Test

This methane to methanol conversion was conducted according to direct route by partial oxidation reaction. A batch reactor with a capacity of 500mL was used to carry out the reaction at 150°C, initial pressure 4 bar for 1 hour. This research will compare the reaction without catalyst, using commercial available ZSM-5 catalyst, synthesized ZSM-5 catalyst, impregnated commercial and synthesized ZSM-5 with Fe and Co. These reactions use 1 g catalyst and 10mL absolute ethanol as solvent. The products in this study were analyzed using GC-FID, their liquid and gaseous forms, with this condition: injector temperature 150°C, detector temperature 200°C and temperature of column is 40°C for 5 min and then ramped from 40 to 170 at 5°C/min and then hold for 10 min. Mix of Porapak Q and Porapak N column was used in this GC analysis. The methanol yield was calculated by interpolating the product's chromatogram's methanol area on the methanol standard curve.

3. Result and discussion

3.1 X-Ray Diffraction (XRD)

The diffractogram of pre-treated CFA and RHA are shown in Fig.1. It shows a CFA pattern that confirms the identity of silica in the form of quartzand also contains iron oxide in the form of hematite and mullite. In the other hand, the RHA pattern confirms the presence of amorf silica.

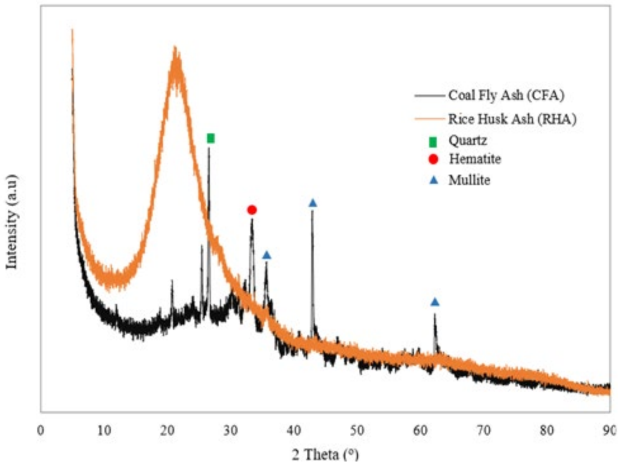


Fig. 1: XRD pattern of pre-treated raw materials CFA and RHA.

The XRD method was applied to confirm the occurence of ZSM-5 framework by comparing the diffractogram of synthesized zeolite catalyst samples to the XRD appearance of ZSM-5 structure from the IZA database. Fig. 2 displays the outcomes of XRD analysis of several synthesized and commercial samples of ZSM-5 within this research. All of the diffractograms of ZSM-5 samples shown in Figure 2 contain distinct and strong peaks at $2\theta = 7\text{-}9^\circ$ and $2\theta = 23\text{-}25^\circ$ area, which match to the structure of ZSM-5 from the IZA database[9,11,12] which fits to the ZSM-5 configuration in the research done by Jiang et al., (2017)[13] and Omar et al., (2018)[14]. These findings affirmed that ZSM-5, both synthetic and commercial samples examined in the XRD inspection have a ZSM-5 zeolite structure. Fig. 2 also showed that the diffractogram of the Fe and Co-impregnated ZSM-5 did not differ significantly from the diffractogram of the ZSM-5 that were not impregnated with Fe and Co. This phenomenon implies that the crystalline framework of ZSM-5 zeolite was maintained despite being impregnated with Fe and Co[13] and there is no metal oxide phase segregation in the impregnated ZSM-5 samples[14].

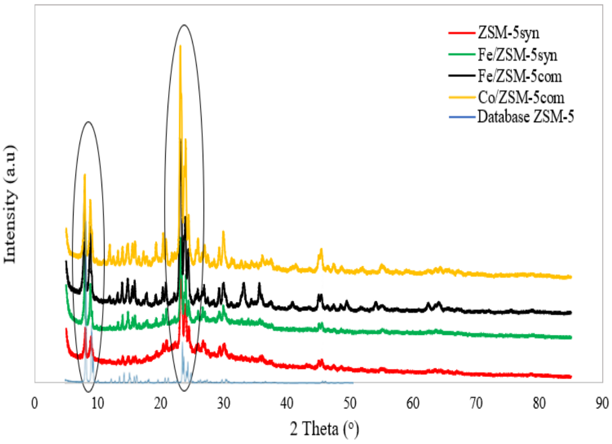


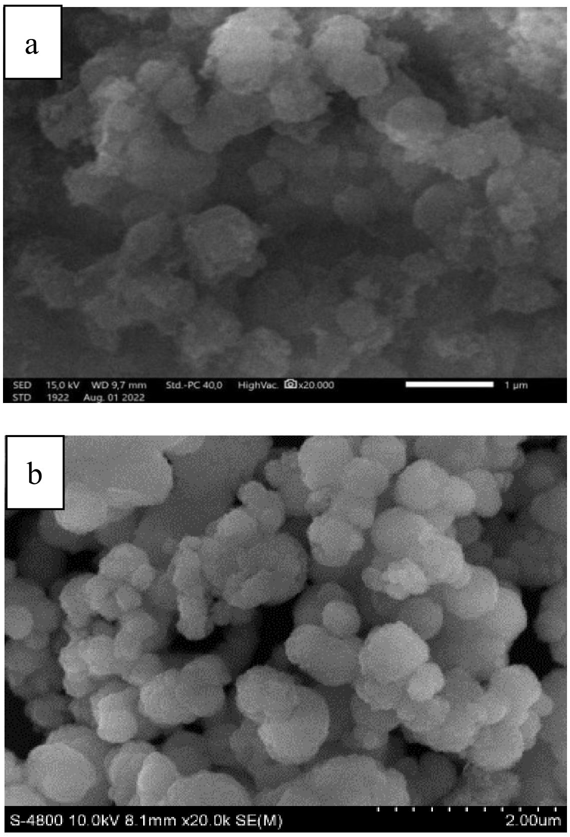
Fig. 2: XRD pattern of synthesized ZSM-5 in comparison to impregnated ZSM-5 and ZSM-5 from the IZA database.

The diffractogram results of some samples also reveal several small peaks in areas of 2θ= 44.8° and 66°15) that are identified as Fe, as well as several small peaks in areas of 2θ = 35.7° and 44.5°16) that are identified as Fe oxides, however these peaks are so weak that they cannot be seen clearly in the Fig. 2.

While for Co components, the peaks exist at 44° and 77°, with the Co oxides appearing at 31.5° and 36.8°17). Again, because of the low intensity of these Co peaks, it is difficult to recognize them in the diffractogram. According to Jimmy et al (2019)'s study18), the intensity of Fe and Co as well as their oxides might be influenced by the amount of the material impregnated to the zeolites, and the close peaks of Fe and Co at 44.8° and 44° give some vague descriptions19). However, the appearance of these peaks indicates that the impregnation of Fe and Co components was done successfully in this research20).

3.2 SEM – EDX

The SEM-EDX morphology of commercially available ZSM-5 crystal structures and those that were synthesized is displayed in Figure 3. The crystal forms of the commercial and synthesized ZSM-5 structures are reveals in Figs. 3(a) and 3(b). While, the elemental distribution in the synthesized structure is shown in Fig. 3(c).



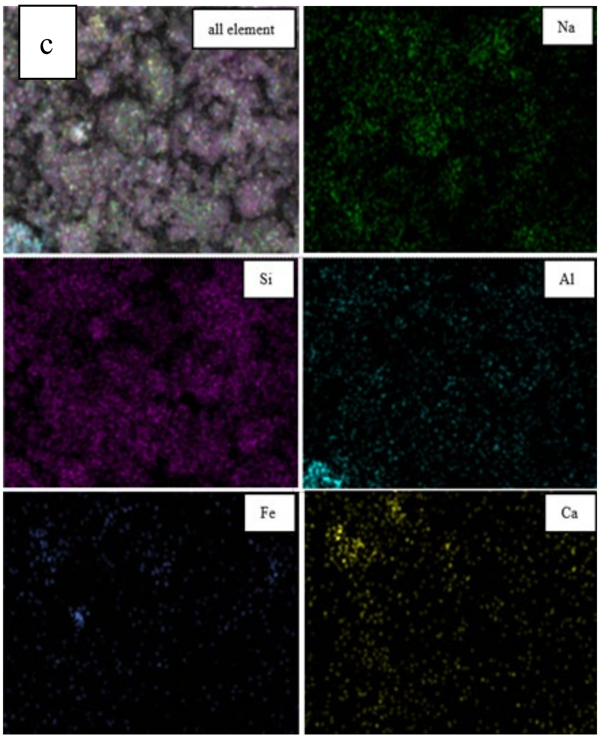
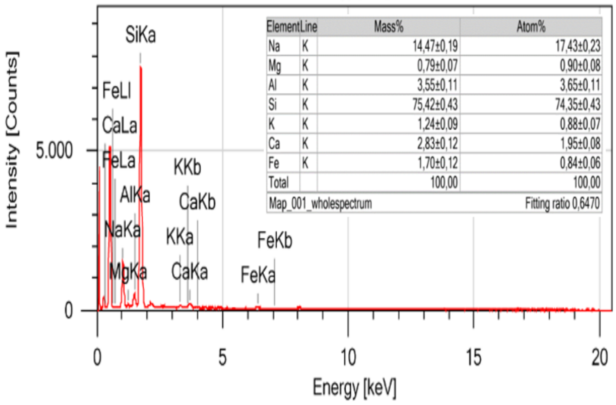


Fig. 3: SEM : (a) ZSM-5$_{\text{syn}}$, (b) ZSM-5$_{\text{com}}$, (c) element distribution of ZSM-5$_{\text{syn}}$.

Fig. 3(a) displays the crystal form of the synthesized ZSM-5, which is identical to the crystal shape of the commercial ZSM-5 in Fig. 3(b), both of which show a coffin shape crystal. This provides more evidence that synthesized ZSM-5 possesses zeolite structure of ZSM-5. The presence of residual impurities in the crystals that may exist due to the utilization of natural materials (CFA as well as RHA) 21) may be inferred from the smudge-like appearance of the synthesized ZSM-5 in the SEM image (Fig. 3(a), even though a pretreatment process has been carried out. However, the clear and firm shape of the ZSM-5 crystals can be caused by various factors such as the ratio of Si/Al, crystallization temperature, raw materials used, and other process conditions during zeolite synthesize9). Fig. 3(c) shows the Sodium (Na) element distribution into the synthesized zeolite framework due to the addition of NaOH during the zeolite synthesis while Fe and Ca comes from the utilization of natural materials used for synthesis. The good stirring and mixing process during zeolite synthesis resulted in homogeneous distribution of particles, which is indicated by relatively even element distribution as shown in Fig. 3(a).

The EDX result of as-synthesized ZSM-5$_{\text{syn}}$ zeolite catalyst was shown in Fig. 4, indicates the type of element and its percentage in the catalyst. The percentage of Si is 75.42%, while the Al element is 3.55%, which agrees with the high loading of Si in the synthesize process. The result of EDX can also be used to confirm the ratio of Si/Al in the as-synthesized catalyst in order to compare the ratio with the synthesis formula. The Si/Al ratio from EDX mapping is 20.41, lower than the formula. The difference between Si/Al ratio with the synthesis formula is normally occurred due to the limitation range in SEM-EDX test, but, the ZSM-5 catalyst that was synthesized still complies with the desired range. In addition, the appearance of other elements in small amounts also indicates the presence of impurities in the catalyst which may be left over from the pre-treatment process of raw material[22,23)].



Element	Line	Mass%	Atom%
Na	K	14,47±0,19	17,43±0,23
Mg	K	0,79±0,07	0,90±0,08
Al	K	3,55±0,11	3,65±0,11
Si	K	75,42±0,43	74,35±0,43
K	K	1,24±0,09	0,88±0,07
Ca	K	2,83±0,12	1,95±0,08
Fe	K	1,70±0,12	0,84±0,06
Total		100,00	100,00
Map_001_wholespectrum			Fitting ratio 0,6470

Fig. 4: EDX analysis of as-synthesized ZSM-5_{syn}.

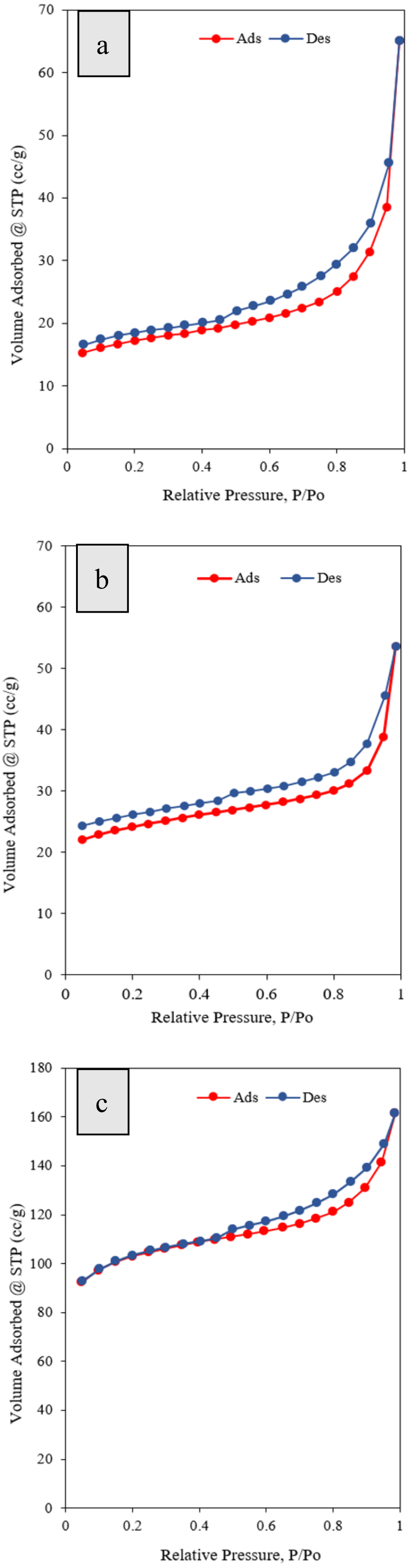
3.3 BET surface area analyzer

The findings of ZSM-5's surface area assessments are compiled in Table 1, and Fig. 5 shows the isotherm adsorption-desorption curves. Quantachrome Novatouch LX2 Surface Area and Pore Size analyzer apparatus were used to measure the area surface of both as-synthesized ZSM-5 and ZSM-5, and the results were displayed in Table 1.

Table 1. BET analyzer results

Catalyst	**The area of spesific surface, m^2/g**	**Total volume of pores, cm^3/g**	**Mean pore size diameter , nm**
ZSM-5_{com}	306.686	0.2518	3.24
Fe/ZSM-5_{com}	291.853	0.2473	3.38
Co/ZSM-5_{com}	291.504	0.2389	3.26
ZSM-5_{syn}	114.870	0.1699	18.81
Fe/ZSM-5_{syn}	72.473	0.0830	4.58

The synt-ZSM-5 was lower surface area than that of commercial one. The impurities from row material such as CFA and RHA may affect to the synthesized of ZSM-5 and could as inhibitor in zeolitization process[22,23)]. ZSM-5 commercial have specific surface area is 306.686 m^2/g, and as-synthesized ZSM-5 have specific area is 114.87 m^2/g. It is clear from examining Table 1 that the total area of specific surface was affected by the alterations of Fe and Co content in ZSM-5. When considering the relative differences with the commercial ZSM-5, the surface areas of both commercial Fe/ZSM-5 and commercial Co/ZSM-5 were smaller. The synthesized Fe/ZSM-5 has a smaller area of surface than ZSM-5_{syn}.



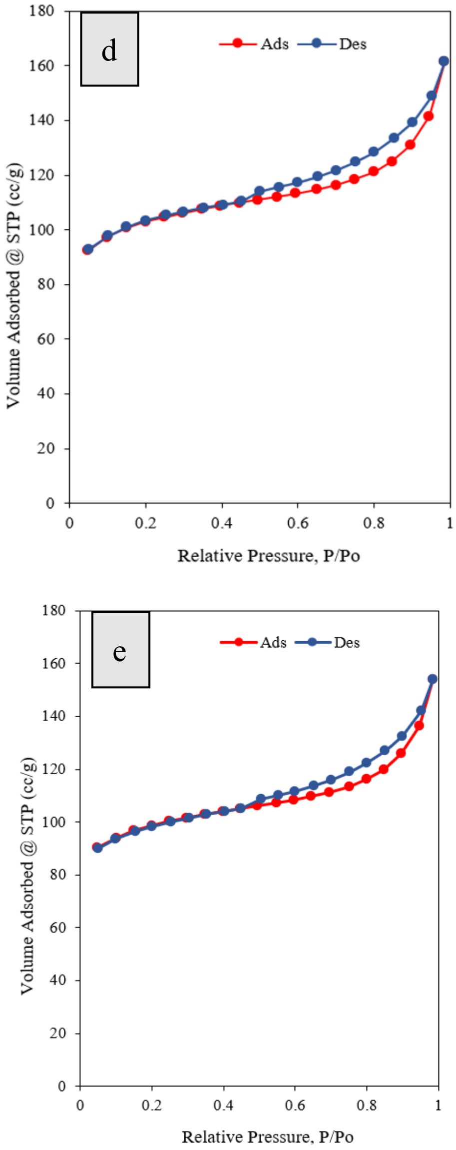


Fig. 5: The isotherm adsorption-desorption curves of (a) ZSM-5_{syn}, (b) Fe/ZSM-5_{syn}, (c) ZSM-5_{com}, (d) Fe/ZSM-5_{com}, and (e) Co/ZSM-5_{com}.

The IUPAC classified porous adsorbents into three types materials based on their pore widths: Pore sizes range more than 50 nm in macroporous, from 2 to 50 nm in mesoporous, and from 0.3 to 2 nm in microporous[24)]. Table 1 reveals that all commercial ZSM-5 and synthesized ZSM-5 are mesoporous, which can be affected by the Si/Al ratio[25)]. For gas-phase adsorption in particular, the relationship between pore size and surface area and, consequently, adsorbent capacity exists. Only materials having mesopores are practical adsorbents with enough surface area for gas-phase applications because the overall surface area of a given quantity of adsorbent rises with decreasing pore size. Table 1. also shown the average pore size diameters of as-synthesized ZSM-5 higher than commercial of ZSM-5 because the as-synthesized ZSM-5 has a target synthesis from coal fly ash and rush husk ash is mesopore ZSM-5 catalyst, so as-synthesized ZSM-5 has pore size diameters higher than commercial of ZSM-5.

The isothermal adsorption-desorption curves of the synthesized ZSM-5, commercial and also the impregnated of those catalyst are shown in Fig. 5. The figures shows that the catalysts have isotherm type curves, which confirms the mesoporous classified materials[26)], in accordance with the pore diameters shown in Table 1. Furthermore, the N_2 isotherm adsorption of the catalysts in Fig. 5 are classified as IV H4 curve type that implied mesoporosity in the material which have a curve with a loop hysteresis shape which is the typical characteristic of type IV isotherm curves, that indicates the presence of mesoporous (IUPAC)[27)]. Every catalyst has different the loop hysterisis shape because every catalyst has different range average pore size diameters too. The commercial-ZSM-5, commercial of Fe/ZSM-5 have similar loop hysterisis shape because they have same range average pore size diameters, and as-synthesis ZSM-5 has loop hysterical shape like Fig. 5 because it has range average pore diameters higher than ZSM-5 commercial.

3.4 Catalytic Performance Test

The effectiveness of ZSM-5 to catalyze methane conversion was evaluated in a 500 ml stainless steel autoclave with a pressure and temperature controller. The ZSM-5 catalyst was activated prior to the reaction at 500 ºC. This activation was aimed to form iron oxide (Fe/ZSM-5) and cobalt oxide (Co/ZSM-5).

The autoclave's chamber was cleansed with nitrogen as an inert gas before being used as the reactor to eliminate organic impurities, evaporated water, and undesired oxygen. The reaction ran for 60 minutes at CH_4 initial pressure of 4 bar and a temperature of 423 K.

Table 2. %Yield Methanol.

No.	Catalyst	Yield (%)
1	No Catalyst	0.45
2	ZSM-5_{com}	2.60
3	Co/ZSM-5_{com}	4.84
4	Fe/ZSM-5_{com}	0.81
5	ZSM-5_{syn}	10.04
6	Co/ZSM-5_{syn}	2.44
7	Fe/ZSM-5_{syn}	13.12

According to Table 2, the synthesized ZSM-5 catalysts resulted in a higher conversion rate than the commercial ZSM-5 catalysts and control sample (without catalyst), since the synthesized ZSM-5 still contains metal oxidic like Fe_2O_3, Mg_2O_3, Na_2O, CaO species at the zeolite outer surface. The ZSM-5 material's effectiveness as a catalyst is observed to be affected by the Fe and Co modifications. Methanol was generated in a yield of 2.6% using the commercial ZSM-5 in the absence of metal oxides, whereas methanol was produced in a yield of 10.04% using the synthesized ZSM-5 in the absence of metal oxides. Based on these findings, we may conclude that increasing the amount of metal oxide increases catalytic activity of methane to methanol partial oxidation reaction. Since the yield of methanol increased when the majority of the metal oxides[28)] were impregnated into ZSM-5, this demonstrates that metal oxides are capable of functioning as productive sites for these catalysts[29)].

Following is the step-by-step procedure that describes the partial oxidation reaction that transformed methane into methanol[7)]:

Step 1, C-H activation

$$Fe/Co - ZSM - 5 + \frac{1}{2}O_2 \rightarrow OFe/Co - ZSM - 5$$

Step 2, hydroxy formation

$$OM - ZSM - 5 + CH_4 \rightarrow \bullet(HO) - Fe/Co - ZSM - 5 + \bullet CH_3$$

Step 3, methanol formation

$$(\bullet \mathrm{HO}) - \mathrm{Fe/Co} - \mathrm{ZSM} - 5 + \mathrm{CH_3} \rightarrow (\mathrm{CH_3}) - (HO) - \mathrm{M} - \mathrm{ZSM} - 5$$

Step 4, desorption of methanol

$$(\mathrm{CH_3}) - (\mathrm{HO}) - \mathrm{Fe/Co} - \mathrm{ZSM} - 5 \rightarrow (\mathrm{CH_3OH}) - \mathrm{Fe/Co} - \mathrm{ZSM} - 5$$
$$(\mathrm{CH_3OH}) - \mathrm{Fe/Co} - \mathrm{ZSM} - 5 \rightarrow \mathrm{Fe/Co} - \mathrm{ZSM} - 5 + \mathrm{CH_3OH}$$

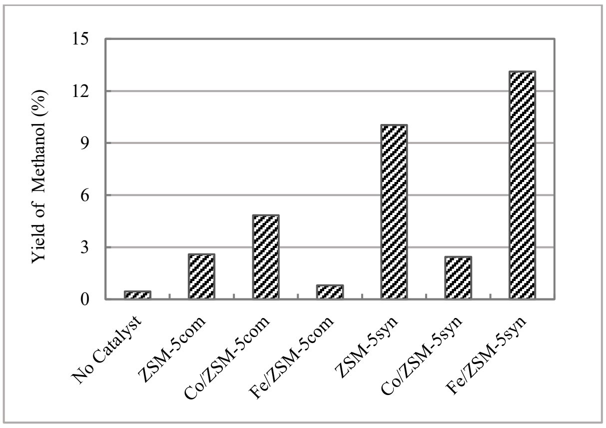


Fig. 6: % Yield of methanol.

Fig. 6 displays that the impregnation of Fe on the as-synthesized ZSM-5 zeolite giving more effect on increasing the yield of methanol compared to Co impregnation. The maximum yield of methanol was achieved by using Fe/ZSM-5_{syn} with the value of 13.12% while ZSM-5_{syn} giving 10.04% yield of methanol.The impregnation of most iron oxides in ZSM-5 increased the % yield of methanol, which indicates that the iron oxide is capable of being the active site of the catalyst, thereby increasing the catalytic activity for oxidizing methane to methanol.

Conclusion

In this work, ZSM-5 zeolite catalyst was successfully synthesized from CFA and RHA utilizing a non-template approach, which is confirmed from XRD, SEM-EDX, and Surface area analyzer characterization. The Iron (Fe) and Cobalt (Co) are successfully impregnated into ZSM-5 zeolite catalyst, confirmed by the appearance peaks of that elements in the diffractogram. Additionally, the impregnation procedure preserves the crystal structure of the material with the distinct peaks of ZSM-5. The frame of as-synthesized ZSM-5_{syn} reveals the characteristic coffin-like structure of the ZSM-5 zeolite catalyst.

Metanol's highest results were achieved with Fe/ZSM-5_{syn} with the value of 13.12% while ZSM-5syn giving 10.04% yield of methanol. Impregnation of Fe and Co in ZSM-5 has affected the catalytic performance test of ZSM-5. Fe impregnation on synthesized ZSM-5 zeolite gives more effect on increasing yield of methanol compared to Co impregnation.

Acknowledgements

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