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Brief Study of Metal-substituted ZSM-5 -Potential Application in Methanol Production

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ABSTRACT

This article clarifies the potential of Zeolite Socony Mobil-5 (ZSM-5) substituted metals such as Copper (II) (Cu) and Iron (III) (Fe) as a catalyst in the methane oxidation reaction to methanol. The authors described the physical and chemical characteristics of modified ZSM-5 with Cu and Fe as well as the fundamental theory in predicting the reaction mechanism and performance of the catalyst active site which is crucial to producing methanol from methane. Methanol has a high economic value and supplies the essential raw materials in energy, petrochemical, pharmaceutical, and environmental industries. Therefore, it is very necessary to have this basic knowledge to increase the efficiency and effectiveness of catalyst performance and enhance the green production process. The reason behind the widely used modified ZSM-5, it was easily applied in the low and intermediates temperature range, and the structure was easy to modify according to the desired performance.

Keywords: Zeolite, methane, methanol, ZSM-5, catalyst

Introduction

The presence of methane (CH_4) with a percentage of more than 55 to 90% can be found in biogas and natural gas, but in impure phases (Qian et al., 2017). Some impurity gases with low concentrations such as carbon dioxide (CO_2), nitrogen (N_2), and hydrogen sulfide (H_2S) contributed to a high loss impact of yield and damage to reactors and pipes which required more complicated maintenance. The utilization of methane in its raw phase also does not provide significant advantages compared to complex gas purification processes. Methane is incompressible so its use really can only be done in the gaseous phase. Transportation constraints mean that the most effective and efficient utilization can only be done if it is close to natural gas sources which are still far from residential areas. In addition, the largest CH_4 and CO_2 emitting countries/regions showed a decrease in emissions in 2016, but Indonesia still experienced the largest absolute increase of 6.4% (de Oliveira et al., 2018; Fakayode et al., 2014).

Zeolite-based membrane technology provided appropriate technology to reduce CH_4 and CO_2 emissions and showed promising features compared to conventional adsorption processes (Zhang et al., 2013). Another function of zeolite-based membranes is as a conversion catalyst to produce more valuable products such as methanol and long-chain hydrocarbons (Demirbas, 2008). However, fabricating membranes is not an easy thing to do, so it is very important to carry out optimization studies in their fabrication, especially in parameter conditions. This is due to the possibility of interaction of the raw material, leakage, and changes in the basic structure after the treatment during fabrication such as stirring, coagulation, and sintering process (Nurherdiana et

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al., 2019). In addition, studies on the utilization of absorption both gases then convert into methanol simultaneously using membrane technology have not been previously reported.

Therefore, it is necessary to study the potential of metal-modified zeolites such as ZSM-5 with other metals as a simultaneous absorbent and catalyst for methanol production from methane. This is an attempt to dig deeper into the chemical and physical properties of catalysts, especially those modified by metals such as Cu and Fe, which have been widely studied. However, there is no summary of studies in distinguishing the characteristics, especially the discussion on synthesis and characterization.

Results and Discussion

The metal substituted in the support material such as ZSM-5 acts as an active site in the methanol-producing reaction. In the mechanism of direct methanol synthesis from methane (DMTM) a methane monooxidase (MMO) enzyme is formed which can oxidize CH bonds in methane and molecular oxygen splitting occurs in the metal center followed by the addition of one oxygen atom in methane (Sharma et al., 2020). Several types of metals that have been used in the methanol-producing reaction were (Beznis et al., 2010; Burnett et al., 2019; Sheppard et al., 2014), Fe (Hammond et al., 2013; Sriakkarin et al., 2018; Starokon et al., 2013), Co, Ni (Mahyuddin et al., 2016), Ga, Zn, In, Mo (Choudhary et al., 2005), Au, Cu, Pd (Ab Rahim et al., 2013). This review will discuss specifically the synthesis of Cu and Fe in ZSM-5 and their role in the reaction of methanol formation. As has been reported by Starokon et al (Starokon et al., 2013; 2011) wherein the partial oxidation reaction of methane using Fe-ZSM-5 and N_2O as oxidizing agents will form α-oxygen sites.

The α-oxygen sites were highly reactive and similar to the O- and OH• radicals. The α-oxygen sites center in Fe-ZSM-5 is postulated as a bis(μ-oxo) di-iron (IV) unit and acts as the active site in the DMTM reaction. The presence of an active site of α-oxygen resulted in irreversible consumption of methane on the surface of the catalyst and formed methoxy species that are strongly bound to the surface. In Cu-ZSM-5, the $[Cu2(\mu\text{-}O)]^{2+}$ site was reported as the active site in the DMTM reaction which can be activated in the presence of N_2O as an oxidizing agent. Metal substitution methods have been carried out through several methods as summarized in Table 1. In this review, two methods commonly used in metal substitution will be discussed, namely solid-state ion exchange and the impregnation method.

Table 1. Synthesis of Cu and Fe modified ZSM-5 catalyst in methanol production reaction

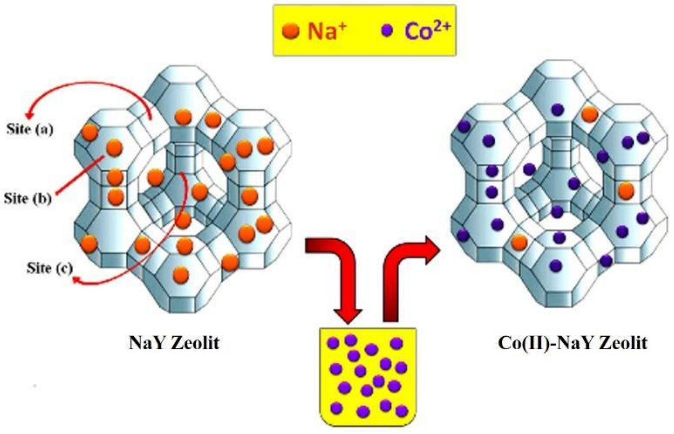
Catalyst	Synthesis Method		Reactor	Reaction Condition	Ref.
	Raw Material (as support)	Substitution Method			
Cu-ZSM-5	Commercial NH_4-ZSM-5	Liquid Phase Ion Exchange (LPIE)	Packed bed reactor	T= 200 °C, P= 1 atm, v_{gas}= 150 mL/min	(Burnett et al., 2019)
Cu-Fe/ZSM-5	Commercial Precursore, T= 240 °C, t= 24 h	Incipient Wetness Impregnation (IWI)	Packed bed reactor	GHSV= 12000 mL/h, P= 10 Bar, T= 180-260 °C	(Sriakkarin et al., 2018)
Cu-Fe/ZSM-5	Commercial NH_4-ZSM-5	Chemical Vapour Impregnation (CVI)	Continuous flow fixed bed	P= 10-30 Bar, T= 25-75 °C	(Xu et al., 2016)

To be continued

Cu-Fe-ZSM-5	Commercial NH_4-ZSM-5	Solid State Ion-Exchange (SSIE)	Batch reactor	T= 50 °C, 1500 rpm	(Hammond et al., 2013)
Cu-ZSM-5	Commercial NH_4-ZSM-5	Liquid Phase Ion Exchange (LPIE)	Batch reactor	T= 150 °C	(Beznis et al., 2010)
Cu/Fe-ZSM-5	Commercial NH_4-ZSM-5	Solid State Ion Exchange (SSIE) dan Wetness Impregnation (WI)	Batch reactor	T= 50 °C, 1500 rpm	(Kalamaras et al., 2016)
Cu-ZSM-5	Commercial NH_4-ZSM-5	Liquid phase ion exchange (LPIE)	Batch reactor	T= 50 °C	(Sheppard et al., 2014)

Solid-State Ion Exchange (SSIE) Method

Zeolite is a hydrated aluminosilicate crystal with a three-dimensional structure of $[AlO_4]^{5-}$ and $[SiO_4]^{4-}$ which are interconnected in the presence of oxygen. The substitution of Al^{3+} and Si^{4+} in the zeolite framework provided a negative charge on the aluminosilicate framework lattice which can be offset by the presence of extra-framework balancing cations such as Na^+, $K^{+,}$ and Ca^{2+}. The cations in the zeolite can be exchanged for other metal ions (Tekin & Bac, 2016). Several studies have been carried out to replace the balancing cations in the zeolite with other cations. The schematic representation of metal ions that replace ions in the zeolite is shown in Figure 1. In a study conducted by Sanaeepur et al (2016), Co^{2+} ions replaced the position of Na^+ ions in the zeolite framework. In a study conducted by Li et al (Li et al., 2019), the exchange of protons in H-ZSM-5 with alkaline ions (Li^+, $Na^{+,}$ and K^+) significantly reduced the number of Brönsted acid sites and increase the number of Lewis acid sites. This cation exchange method was carried out by making a solution of $LiOH.H_2O/NaOH/KOH$ and H-ZSM-5 was added to the solution and stirred for 3 hours at a temperature of 60 °C.



Co^{2+} Solution

Figure 1. Schematic representation of Co^{2+} ions when replacing N^{a+} ions in a zeolite framework (Sanaeepur et al., 2016)

Another study was conducted by Burnett et al (Burnett et al., 2019) in which protons in H-ZSM-5 were exchanged for cations with Cu^{2+} metal through the wet ion-exchange method. Commercial NH_4-ZSM-5 was calcined at 500 °C (1 °C/min) for 8 hours to form H-ZSM-5. Cu $(NO_3)_2$ solution used as Cu^{2+} ion precursor was added to H-ZSM-5 and stirred for 24 hours. Cu-ZSM-5 solids were separated by the centrifugation method. One of the characterization instruments that can be used to identify the formation of Cu-ZSM-5 is using XRD as shown in Figure 2. The X-ray diffraction pattern shows the presence of MFI structural characters that appear at 2θ=10.5°,15.8°,16.5°, 17.7 °, 18.6°, 27.4°, 28.4°, 30.2°, and 35.7° which are plane diffraction (111), (102), (112), (131), (022), (051), (313), (323) and (062). Magnification at 2θ= 40-60° did not find intense peaks of CuO which indicated the particle size of CuO was so small that it was not detected on XRD.

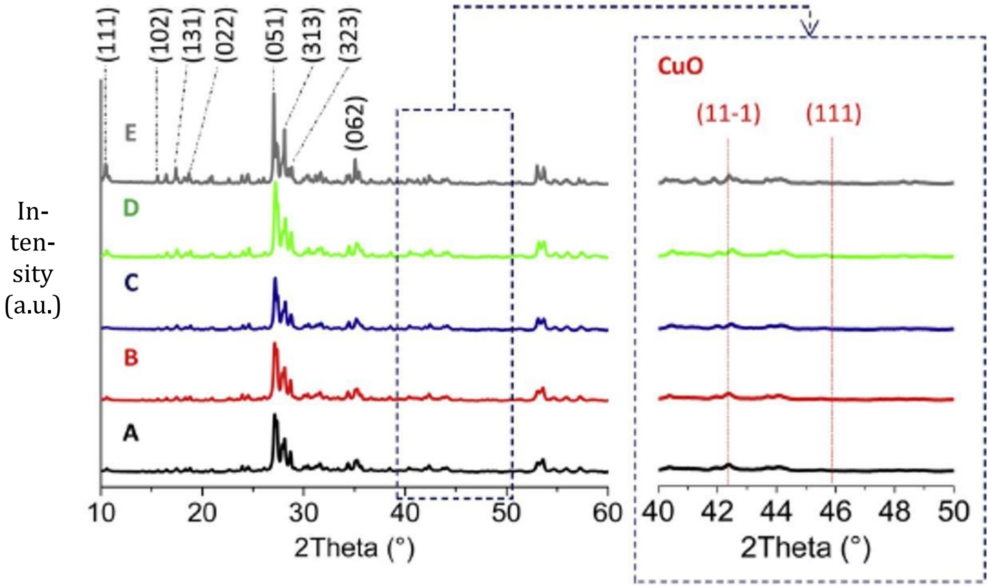


Figure 2. X-ray diffraction (XRD) pattern of Cu-ZSM-5 with various ratios (Si/Al) (A) Cu-ZSM-5 (20:1), (B) Cu-ZSM-5 (30:1), (C) Cu-ZSM-5 (50:1), (D) Cu-ZSM-5 (80:1) and (E) Cu-ZSM-5 (200-400:1) (Burnett et al., 2019)

A similar method was also carried out by Beznis et al (Beznis et al., 2010) by dissolving Na-ZSM-5 with Cu $(CH_3COO)_2$ solution to replace Na^+ cations in ZSM-5. The instrument that can be used to analyze the effect of Cu^{2+} concentration on Cu-ZSM-5 is using UV-Vis NIR as shown in Figure 3. Based on the UV-Vis NIR spectra, two absorption bands are obtained at wavenumbers 14000 and 22700 cm^{-1}. The absorption band at wave number 14000 cm^{-1} is a d-d transition of Cu^{2+} pseudo octahedral. Furthermore, wave number 22700 cm^{-1} is the charge transfer band from Cu to O in the bis(μ-oxo) dicopper or mono-(μ-oxo) dicopper species. The intensity of the absorption peak increased with increasing Cu^{2+} concentration.

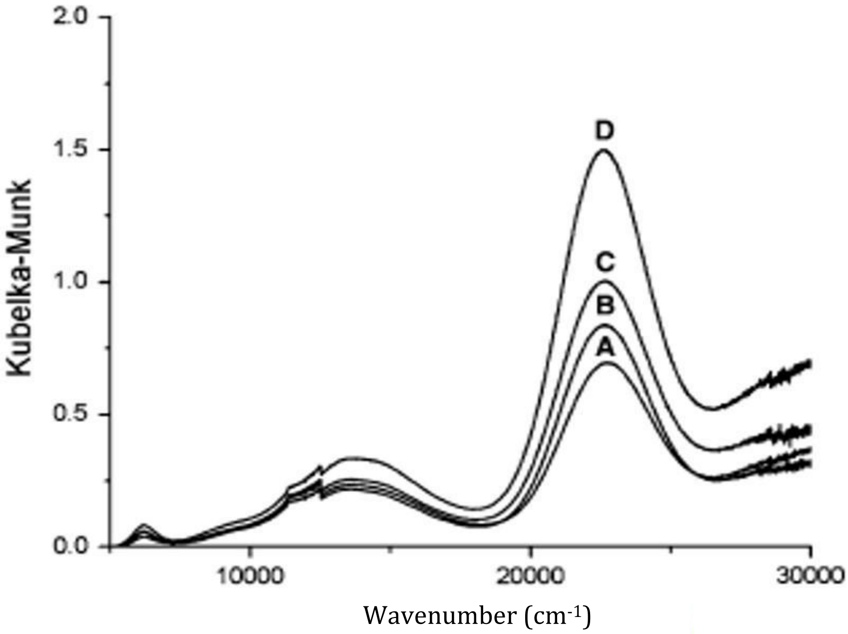


Figure 3. UV–Vis-NIR spectra on Cu-A-2.2 (a), Cu-A-2.4 (b), Cu-A-2.5 (c), and Cu-A-2.6 (d) after calcination at temperature of 550 °C (Beznis et al., 2010)

In addition to the wet ion exchange method, the cation exchange method can also be carried out using the Solid State Ion Exchange (SSIE) method as done by Hammond et al. (Hammond et al., 2013) and Kalamaras et al (Kalamaras et al., 2016). Commercial NH_4-ZSM-5 was previously calcined at 550 °C for 3 hours to form H-ZSM-5. Solid-state ion exchange was carried out by mixing Fe-acetylacetonate ($Fe(C_5H_7O_2)_3$) and H-ZSM-5 and milling for 15 minutes (Hammond et al., 2013). Besides grinding, pestle and mortar can also be used to mix NH_4-ZSM-5 and [Fe(acac)3]/[Cu(acac)2] for 30 minutes. The catalyst obtained was then calcined at a temperature of 550 °C (10 °C /min) for 3 hours (Kalamaras et al., 2016). Acidity analysis on ZSM-5, Cu/ZSM-5, and Fe/ZSM-5 catalysts can be analyzed using the NH_3-TPD instrument as shown in Figure 4. As shown in Figure 4, Cu/ZSM-5 and Fe/ZSM catalysts -5 has a different profile from ZSM-5 which has two desorption peaks at temperatures of 197 and 409 °C which is the contribution of weak acids and strong acids. Weak acids come from weak NH_3 bonds at the Lewis acid site, while strong acids come from NH_4^+ ions where 3 hydrogen atoms are bonded to three oxygen atoms from the AlO_4 tetrahedral from the Brönsted acid site. Substitution of Cu and Fe ions in ZSM-5 significantly reduced the number of strong acid sites indicating a decrease in the number of Brönsted acid sites due to proton substitution in ZSM-5 with Cu^{2+} and Fe^{3+}. This result is following another study conducted by Li et al (Li et al., 2019), where the substitution of cations Li^+, $Na^{+,}$ and K^+ reduced the number of Brönsted acid sites due to the exchange of protons H-ZSM-5 which acts as a Brönsted acid site and replaced with alkaline cation.

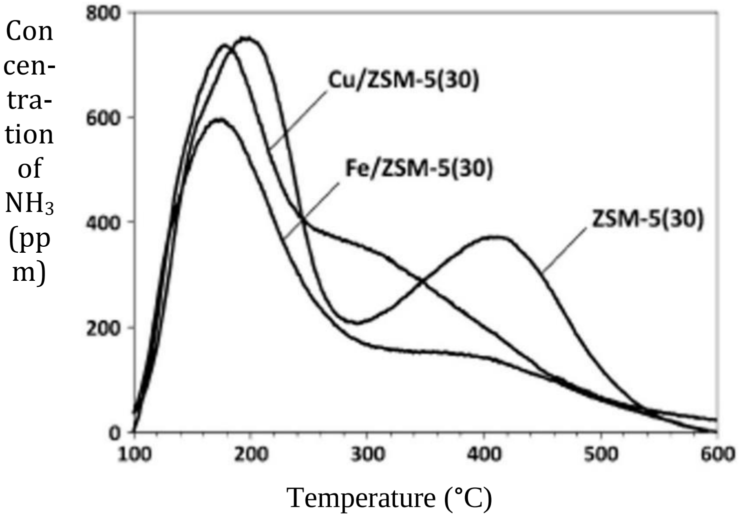


Figure 4. NH_3-TPD profiles of ZSM-5(30), Cu/ZSM-5(30), and Fe/ZSM-5 were synthesized using the SSIE method (Kalamaras et al., 2016)

Impregnation method

Another method that can be used in zeolite modification with the addition of metal is the impregnation technique. Impregnation techniques are classified into two, namely Incipient Wetness Impregnation (IWI) and Wet Impregnation (WI) (Flores et al., 2019). Incipient Wetness Impregnation (IWI) technique or also called dry impregnation involves capillary filling of the pores of the catalyst supported by metal with the addition of a minimum of solvent. This method will generally produce metal with a large size and lower dispersion than the Wet Impregnation (WI) technique. The wet impregnation (WI) method involves the suspension of the supported catalyst in a metal salt solution as a precursor with an excess amount of solvent. Some of the solvents used include methanol, ethanol, and acetone to increase metal diffusion in the supporting catalyst pore system. This wet impregnation method will generally produce a catalyst with a more uniform metal dispersion and a small metal size. The schematic representation of the cobalt metal species on the HBEA and NaBEA catalysts is shown in Figure 5. The metal species deposited on the supported catalyst by the impregnation method can be in the zeolite pore (Figure 5a) or on the zeolite surface (Figure 5b).

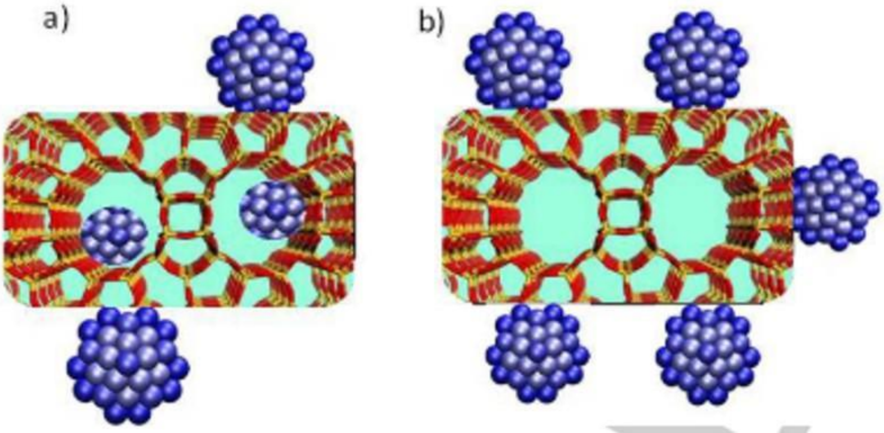


Figure 5. Schematic Representation of Cobalt Species in Co/HBEA and Co/NaBEA (Flores et al., 2019).

Sriakkarin et al. (2018) successfully synthesized ZSM-5 catalyst with the addition of Cu and Fe metals through the dry impregnation method or Incipient Wetness Impregnation (IWI). In the dry impregnation method, Cu $(NO_3)_2 \cdot 3H_2O$ and Fe $(NO_3)_3 \cdot 6H_2O$ are used as metal precursors. The obtained catalyst was then dried using microwave irradiation at 800 W for 3 minutes and followed by calcination in an air atmosphere at 500 °C for 5 hours. Based on the analysis using XRD, it can be seen that the crystallinity of ZSM-5 after the impregnation of Cu and Fe metals decreased by 64%. The metal nanoclusters may enter the pores of the zeolite and spread on the surface of the zeolite. The agglomeration of metal particles can also cause the blocking of the pores of ZSM-5. Similar results have also been reported by Oliveira et al (de Oliveira et al., 2018) where the impregnation of Cu and Fe metals will significantly reduce the crystallinity of ZSM-5. In addition, the absence of diffraction peaks from Fe_2O_3 indicated that the iron deposited on the zeolite was evenly distributed on the surface and pores of the zeolite and had a particle size of less than 4 nm.

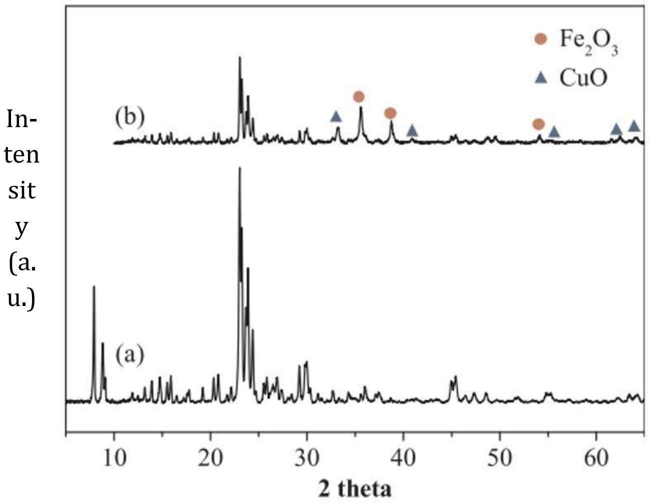


Figure 6. XRD pattern of ZSM-5 (a) and 10Cu-10Fe/ZSM-5 (b) (Sriakkarin et al., 2018)

Another study was conducted by Kalamaras et al (2016) who successfully synthesized Cu/ZSM-5 using the wet impregnation (WI) method. In the wet impregnation method used solutions of $Cu(acac)_2$, $CuCl_2$, $Cu(NO_3)_2.3H_2O$ as metal precursors. The excess solvent used in this wet impregnation method was then evaporated at a temperature of 70 °C for 4 hours. The resulting solid was then dried at a temperature of 120 °C overnight and calcined at a temperature of 550 °C (10 °C/min) for 3 hours. The X-ray diffraction pattern of Cu/ZSM-5 is shown in Figure 7. Cu/ZSM-5 catalyst synthesized with various metal precursors showed no significant changes in the characteristic peaks of ZSM-5 which indicated no segregation of the CuO phase. In addition, there were no characteristic peaks of CuO at $2\theta = 35.6°$ and $38.7°$ which indicated that CuO was evenly distributed on the surface and pores of the zeolite. Lima and Perez-Lopez (2019) also reported the deposition of Fe, Mo, and Nb metals on ZSM-5 by the wet impregnation method. The results of the analysis showed that after impregnation of Fe, Mo, and Nb metals, there were no characteristic diffraction peaks of metal oxides which indicated an even metal dispersion on the zeolite surface.

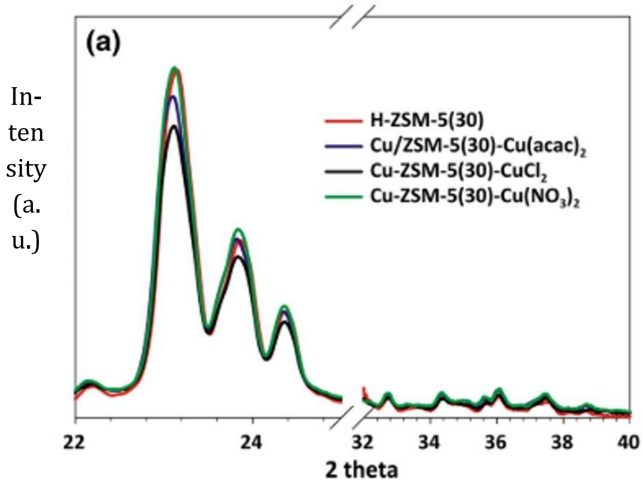


Figure 7. X-ray diffraction (XRD) pattern of Cu/ZSM-5 with various metal precursors.

In addition to the IWI and WI methods which are distinguished by the amount of solvent used, impregnation can also be carried out using the Chemical Vapor Impregnation (CVI) method. The advantage of the CVI method is that it produces a catalyst with high metal dispersion on the zeolite surface and can control metal deposition easily (Forde et al., 2014). Research conducted by Xu et al (Xu et al., 2016), used the CVI method with metal precursors Cu(acac)$_2$ and Fe(acac)$_3$. ZSM-5 and metal precursors were mixed in the flask and stirred without the addition of solvent. The dry mixture was then heated at a temperature of 150 °C and vacuumed (10^{-3} mBar) for 2 hours. The catalyst obtained was then calcined at a temperature of 550 °C (20 °C/min) for 3 hours. The results of the analysis of Cu/ZSM-5, Fe/ZSM-5, and Cu-Fe/ZSM-5 catalysts using 27Al MAS NMR showed that the impregnation of Fe and Cu metals did not affect the MFI framework of ZSM-5. The decrease in the intensity of the resonance signal from the Al tetrahedral site (55 ppm) indicates the presence of paramagnetic Fe and/or Cu species that change the position of the ions in ZSM-5. Cation exchange occurs in the hydroxyl group (SiOHAl) where there is an interaction between the unpaired electrons of the paramagnetic Fe species and the 27Al framework so that it will reduce the intensity of the Al tetrahedral signal.

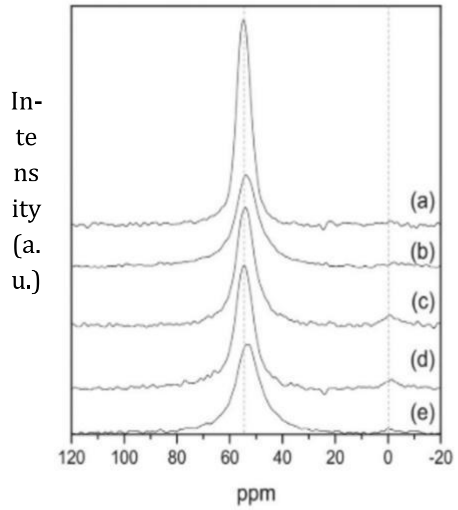


Figure 8. ^{27}Al MAS-NMR Spectra of (a) H-ZSM-5 (30), (b) 1.5% Cu/ZSM-5 (30), (c) 1.5% Fe/ZSM-5 (30), (d) 0.4% Fe 0.4% Cu/ZSM-5 (30) dan (e) 1.5% Fe 1.5% Cu/ZSM-5 (30) (Xu et al., 2016)

Conclusion

In this brief review, the modified ZSM-5 with metal ion has been successfully used as a catalyst material to convert methane into a more value-added chemical product, such as methanol. Na^+ cations were connected in a framework that functions as a stabilizer for the crystal structure and acid sites of zeolite. There are two acid sites, namely Brönsted and Lewis acid sites. The strength of the two acids can be modified through the substitution of cations such as Cu and Fe ions, the percentage added, and the different synthesis methods. In current literature, the interconnection of metal ions with ZSM-5 structures has been proven by the applied synthesis method, namely solid-state ion exchange (SSIE) and impregnation. The success of the interconnection can be easily determined through basic characterizations such as x-ray diffraction (XRD) through analysis of the diffraction peak at 2 theta as the presence of metal ion, UV-Vis NIR through absorption band, NH3-TPD contributes to analysis this kind of Lewis and Brönsted acid. As aforementioned, the basic knowledge of the modified ZSM-5 synthesis, characterization, and performance is very crucial to well-understand so that it is easy to optimize its performance.

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