

Brief Study

By Reva Nugraha

WORD COUNT

4395

TIME SUBMITTED

14-OCT-2022 11:04AM

PAPER ID

91549550

Conference Paper

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

Silvana Dwi Nurherdiana^{1*}, Reva Edra Nugraha¹, Rachmad Ramadhan Yogaswara¹, Shanita Agitiya Utama¹, Achmad Naufal Nuraffandy¹, Merry Jhoe Stefhanny Manupapami¹, Hamzah Fansuri²

¹Department of Chemical Engineering, Faculty of Engineering, Universitas Pembangunan Nasional "Veteran" Jawa Timur, Surabaya 60294, Indonesia

²Department of Chemistry, Faculty of Science and Data Analytics, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya, East Java 60111, Indonesia

*Corresponding author:

E-mail:

silvana.dwi.tk@upnjatim.ac.id

ABSTRACT

This article clarifies the potential of Zeolite Socony Molecular Sieves (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 (CH₄) 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 (CO₂), nitrogen (N₂), and hydrogen sulfide (H₂S) 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 CH₄ and CO₂ 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 CH₄ and CO₂ 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

How to cite:

Nurherdiana, S. D. et al. (2022). Brief Study of Metal-substituted ZSM-5 -Potential Application in Methanol Production. *International Seminar of Research Month 2021. NST Proceedings*. pages 316-325. doi: 10.11594/ nstp.2022.2448

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., 2022). 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 N₂O 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(μ-O)]²⁺ site was reported as the active site in the DMTM reaction which can be activated in the presence of N₂O 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 [AlO₄]⁵⁻ and [SiO₄]⁴⁻ which are interconnected in the presence of oxygen. The substitution of Al³⁺ and Si⁴⁺ in 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 Ca²⁺. 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), Co²⁺ ions replaced the position of Na⁺ ions in the zeolite framework. In a study conducted by Li et al (Li et al., 2012), 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.H₂O/NaOH/KOH and H-ZSM-5 was added to the solution and stirred for 3 hours at a temperature of 60 °C.

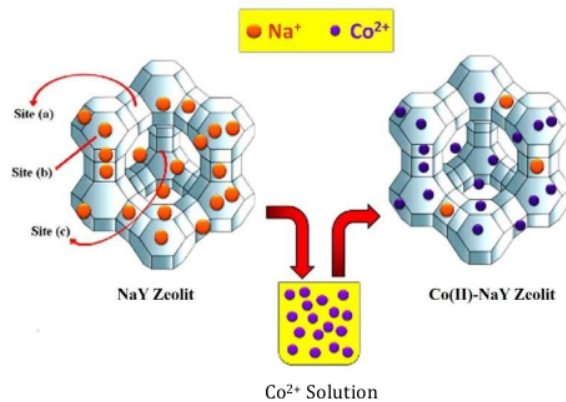
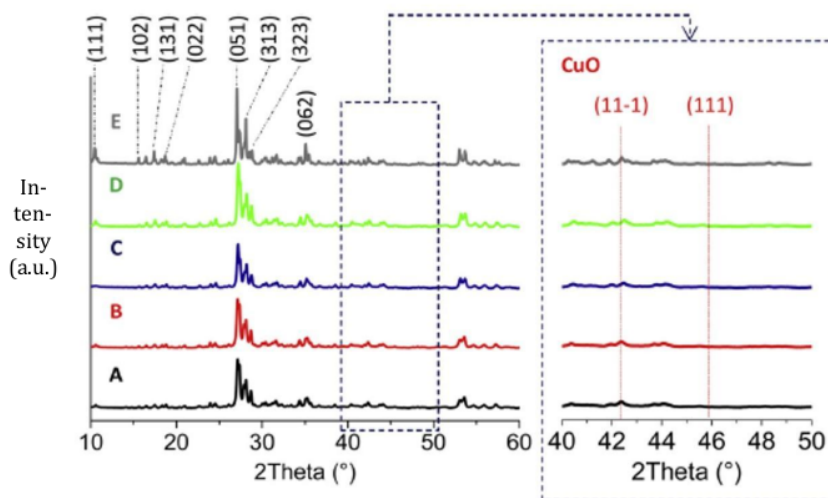


Figure 1. Schematic representation of Co²⁺ ions when replacing Na⁺ ions in a zeolite framework (Sanaeepur et al., 2016)

Another study was conducted by Burnett et al (Burnett et al., 2019) in which protons in H-ZSM-5 were exchanged for cations with Cu²⁺ metal through the wet ion-exchange method. Commercial NH₄-ZSM-5 was calcined at 500 °C (10 min) for 8 hours to form H-ZSM-5. Cu(NO₃)₂ solution used as Cu²⁺ 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 $2\theta=10.5^\circ, 15.8^\circ, 16.5^\circ, 17.7^\circ, 18.6^\circ, 27.4^\circ, 28.4^\circ, 30.2^\circ,$ and 35.7° which are plane diffraction (111), (102), (112), (131), (022), (051), (313), (323) and (062). Magnification at $2\theta=40-60^\circ$ did not find intense peaks of CuO which indicated the particle size of CuO was so small that it was not detected on XRD.



44 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)

38 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 Cu²⁺ 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 Cu²⁺ 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 Cu²⁺ concentration.

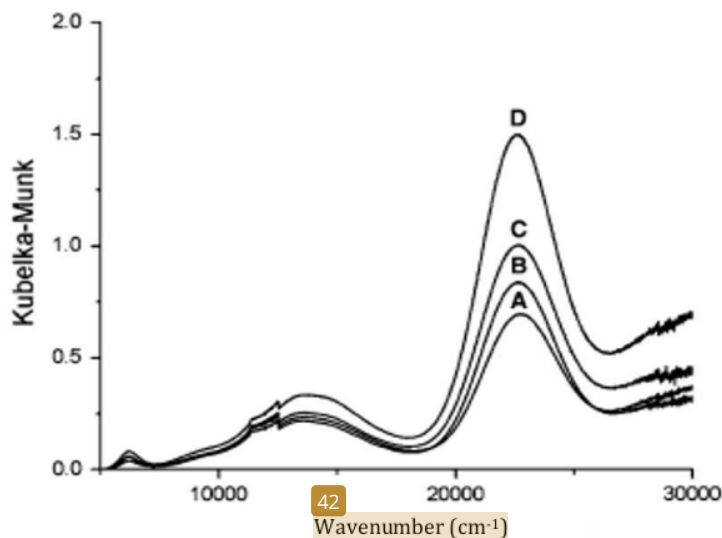


Figure 3. UV-Vis-NIR spectra on Cu-A-2.2 (a), Cu-A-2.4 (b), Cu-A-2.5 (c), and Cu-A-2.6 (d) after calcination at temperature of 550 °C (Beznis et al., 2010)

40
 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 $\text{NH}_4\text{-ZSM-5}$ 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 ($\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$) and H-ZSM-5 and milling for 15 minutes (Hammond et al., 2013). Besides grinding, pestle and mortar can also be used to mix $\text{NH}_4\text{-ZSM-5}$ and $[\text{Fe}(\text{acac})_3]/[\text{Cu}(\text{acac})_2]$ 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 of ZSM-5, Cu/ZSM-5, and Fe/ZSM-5 catalysts can be analyzed using the $\text{NH}_3\text{-TPD}$ instrument as shown in Figure 4. As shown in Figure 4, Cu/ZSM-5 and Fe/ZSM-5 catalysts have 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 in H-ZSM-5 which acts as a Brönsted acid site and replaced with alkaline cation.

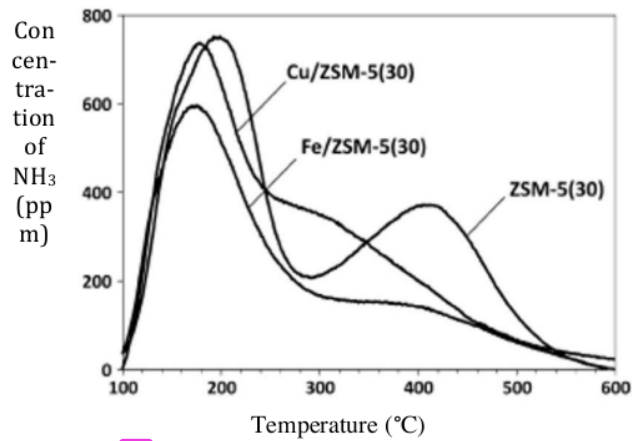


Figure 4. NH_3 -TPD profiles of ZSM-5(30), Cu/ZSM-5(30), and Fe/ZSM-5(30) were synthesized using the SSIE method (Kalamaras et al., 2016)

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).

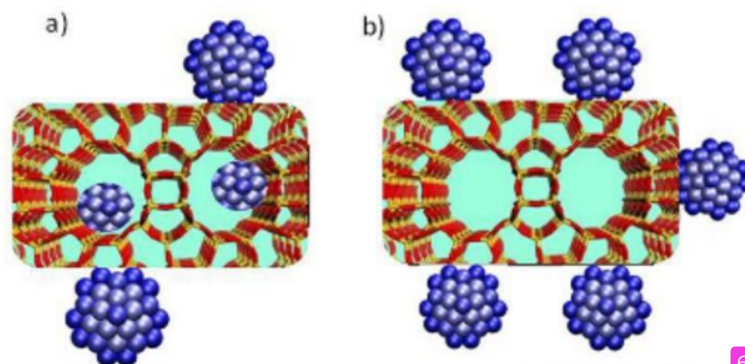


Figure 5. Schematic Representation of Cobalt Species in Co/HBEA and Co/NaBEA (Flores et al., 2019).

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, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 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.

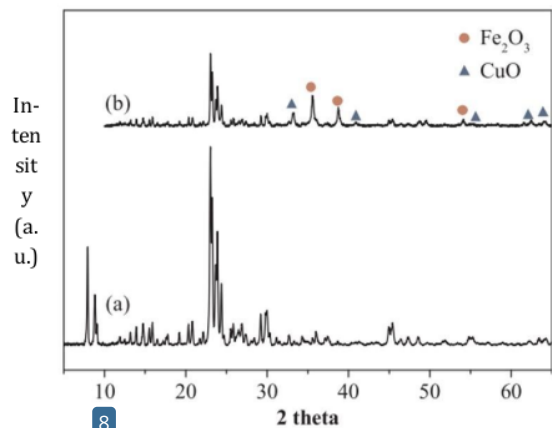
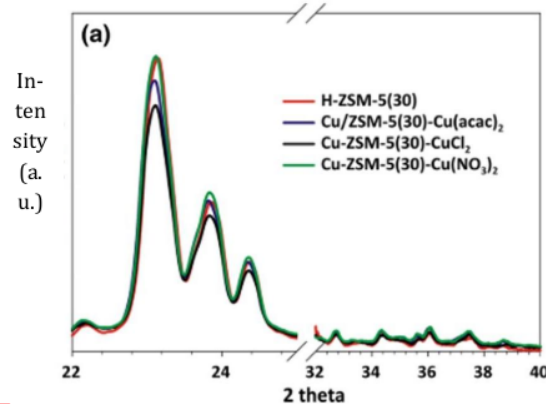


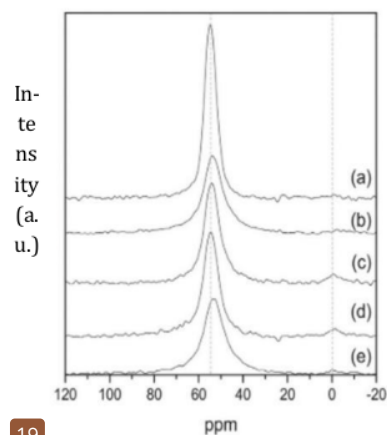
Figure 6. XRD pattern of ZSM-5 (a) and 10Cu-10Fe/ZSM-5 (b) (Sriakkarin et al., 2018)

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 $\text{Cu}(\text{acac})_2$, CuCl_2 , $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ 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 $2\theta = 35.6^\circ$ 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.



25 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 $\text{Cu}(\text{acac})_2$ and $\text{Fe}(\text{acac})_3$. ZSM-5 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 ^{27}Al 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 ^{27}Al framework so that it will reduce the intensity of the Al tetrahedral signal.



19 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 Brønsted 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 Brønsted 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.

45

Acknowledgment

The authors would like to thank Dana Internal UPN "Veteran" Jawa timur Fiscal year 2021 from DIPA UPNVJT with contract number of SPP/13/UN.63.8/LT/IV/2021 for the financial support.

References

- Ab Rahim, M. H., Forde, M. M., Hammond, C., Jenkins, R. L., Dimitratos, N., Lopez-Sanchez, J. A., Carley, A. F., Taylor, S.H., Willock, D. J., & Hutchings, G. J. (2013). Systematic study of the oxidation of methane using supported gold palladium nanoparticles under mild aqueous conditions. *Top. Catal.*, *56*, 1843–1857. <https://doi.org/10.1007/s11244-013-0121-3>
- Beznis, N. V., Weckhuysen, B. M., & Bitter, J. H. (2010). Cu-ZSM-5 zeolites for the formation of methanol from methane and oxygen: Probing the active sites and spectator species. *Catal. Letters*, *138*, 14–22. <https://doi.org/10.1007/s10562-010-0380-6>
- Burnett, L., Rysakova, M., Wang, K., González-Carballo, J., Tooze, R. P., & García-García, F. R. (2019). Isothermal cyclic conversion of methane to methanol using copper-exchanged ZSM-5 zeolite materials under mild conditions. *Appl. Catal. A Gen.*, *587*, 117272. <https://doi.org/10.1016/j.apcata.2019.117272>
- Choudhary, V. R., Mondal, K. C., & Mulla, S.A. R. (2005). Simultaneous Conversion of Methane and Methanol into Gasoline over Bifunctional Ga-, Zn-, In-, and/or Mo-Modified ZSM-5 Zeolites. *Angew. Chemie*, *117*, 4455–4459. <https://doi.org/10.1002/ange.200500694>
- de Oliveira, T. K. R., Rosset, M., & Perez-Lopez, O. W. (2018). Ethanol dehydration to diethyl ether over Cu-Fe/ZSM-5 catalysts. *Catal. Commun.*, *104*, 32–36. <https://doi.org/10.1016/j.catcom.2017.10.013>
- Demirbas, A. (2008). Biomethanol production from organic waste materials. *Energy Sources, Part A Recover. Util. Environ. Eff.*, *30*, 565–572. <https://doi.org/10.1080/15567030600817167>
- Fakayode, S. O., Mitchell, B. S., & Pollard, D. A. (2014). Determination of boiling point of petrochemicals by gas chromatography-mass spectrometry and multivariate regression analysis of structural activity relationship. *Talanta*, *126*, 151–156.
- Flores, C., Batalha, N., Marcilio, N. R., Ordonsky, V. V., & Khodakov, A. Y. (2019). Influence of Impregnation and Ion Exchange Sequence on Metal Localization, Acidity and Catalytic Performance of Cobalt BEA Zeolite Catalysts in Fischer-Tropsch Synthesis. *ChemCatChem*, *11*, 568–574. <https://doi.org/10.1002/cctc.201800728>
- Forde, M. M., Armstrong, R. D., McVicker, R., Wells, P. P., Dimitratos, N., He, Q., Lu, L., Jenkins, R. L., Hammond, C., Lopez-Sanchez, J. A., Kiely, C. J., & Hutchings, G. J. (2014). Light alkane oxidation using catalysts prepared by chemical vapour impregnation: Tuning alcohol selectivity through catalyst pre-treatment. *Chem. Sci.*, *5*, 3603–3616. <https://doi.org/10.1039/c4sc00545g>
- Hammond, C., Dimitratos, N., Jenkins, R. L., Lopez-Sanchez, J. A., Kondrat, S. A., Hasbi Ab Rahim, M., Forde, M. M., Thetford, A., Taylor, S. H., Hagen, H., Stangland, E. E., Kang, J. H., Moulijn, J. M., Willock, D. J., & Hutchings, G. J. (2013). Elucidation and evolution of the active component within Cu/Fe/ZSM-5 for catalytic methane oxidation: From synthesis to catalysis. *ACS Catal.*, *3*, 689–699. <https://doi.org/10.1021/cs3007999>
- Kalamaras, C., Palomas, D., Bos, R., Horton, A., Crimmin, M., Hellgardt, K. (2016). Selective Oxidation of Methane to Methanol over Cu-And Fe-Exchanged Zeolites: The Effect of Si/Al Molar Ratio. *Catal. Letters*, *146*, 483–492. <https://doi.org/10.1007/s10562-015-1664-7>
- Li, M., Xing, S., Yang, L., Fu, J., Lv, P., Wang, Z., Yuan, Z. (2019). Nickel-loaded ZSM-5 catalysed hydrogenation of oleic acid: The game between acid sites and metal centres. *Appl. Catal. A Gen.*, *587*, 117112. <https://doi.org/10.1016/j.apcata.2019.117112>
- Lima, D. S., & Perez-Lopez, O. W. (2019). Catalytic conversion of glycerol to olefins over Fe, Mo, and Nb catalysts supported on zeolite ZSM-5. *Renew. Energy*, *136*, 828–836. <https://doi.org/10.1016/j.renene.2019.01.051>
- Mahyuddin, M.H., Staykov, A., Shiota, Y., & Yoshizawa, K. (2016). Direct Conversion of Methane to Methanol by Metal-Exchanged ZSM-5 Zeolite (Metal = Fe, Co, Ni, Cu). *ACS Catal.*, *6*, 8321–8331. <https://doi.org/10.1021/acscatal.6b01721>
- Nurherdiana, S. D., Utomo, W. P., Sajidah, H. B. N., Jamil, S. M., Othman, M. H. D., & Fansuri, H. (2019). Comprehensive Study of Morphological Modification of Dual-Layer Hollow Fiber Membrane. *Arab. J. Sci. Eng.*, *44*, 10041–10055. <https://doi.org/10.1007/s13369-019-04057-5>
- Qian, Y., Sun, S., Ju, D., Shan, X., Lu, X. (2017). Review of the state-of-the-art of biogas combustion mechanisms and applications in internal combustion engines. *Renew. Sustain. Energy Rev.*, *69*, 50–58.

- Sanaeepur, H., Kargari, A., Nasernejad, B., Ebadi Amooghini, A., & Omidkhah, M. (2016). A novel Co²⁺ exchanged zeolite Y/cellulose acetate mixed matrix membrane for CO₂/N₂ separation. *J. Taiwan Inst. Chem. Eng.*, *60*, 403–413. <https://doi.org/10.1016/j.jtice.2015.10.042>
- Sharma, R., Poelman, H., Marin, G. B., & Galvita, V. V. (2020). Approaches for selective oxidation of methane to methanol. *Catalysts*, *10*. <https://doi.org/10.3390/catal10020194>
- Sheppard, T., Hamill, C. D., Goguet, A., Rooney, D. W., Thompson, J. M. (2014). A low temperature, isothermal gas-phase system for conversion of methane to methanol over Cu-ZSM-5. *Chem. Commun.* *50*, 11053–11055. <https://doi.org/10.1039/c4cc02832e>
- Sriakkarin, C., Umchoo, W., Donphai, W., Poo-arporn, Y., & Chareonpanich, M. (2018). Sustainable production of methanol from CO₂ over 10Cu-10Fe/ZSM-5 catalyst in a magnetic field-assisted packed bed reactor. *Catal. Today*, *314*, 114–121. <https://doi.org/10.1016/j.cattod.2017.12.037>
- Starokon, E. V., Parfenov, M. V., Arzumanov, S. S., Pirutko, L. V., Stepanov, A. G., & Panov, G. I. (2013). Oxidation of methane to methanol on the surface of FeZSM-5 zeolite. *J. Catal.* *300*, 47–54. <https://doi.org/10.1016/j.jcat.2012.12.030>
- Starokon, E. V., Parfenov, M. V., Pirutko, L. V., Abornev, S.I., Panov, G.I. (2011). Room-temperature oxidation of methane by α -oxygen and extraction of products from the FeZSM-5 surface. *J. Phys. Chem. C*, *115*, 2155–2161. <https://doi.org/10.1021/jp109906j>
- Tekin, R., Bac, N. (2016). Antimicrobial behavior of ion-exchanged zeolite X containing fragrance. *Microporous Mesoporous Mater.* *234*, 55–60. <https://doi.org/10.1016/j.micromeso.2016.07.006>
- Xu, J., Armstrong, R. D., Shaw, G., Dummer, N. F., Freakley, S. J., Taylor, S. H., & Hutchings, G. J. (2016). Continuous selective oxidation of methane to methanol over Cu- and Fe-modified ZSM-5 catalysts in a flow reactor. *Catal. Today*, *270*, 93–100. <https://doi.org/10.1016/j.cattod.2015.09.011>
- Zhang, Y., Su, K., Zeng, F., Ding, W., & Lu, X. (2013). A novel tubular oxygen-permeable membrane reactor for partial oxidation of CH₄ in coke oven gas to syngas. *Int. J. Hydrogen Energy* *38*, 8783–8789. <https://doi.org/10.1016/j.ijhydene.2013.05.019>

Brief Study

ORIGINALITY REPORT

22%

SIMILARITY INDEX

PRIMARY SOURCES

- 1 Pieter J. Smeets, Julia S. Woertink, Bert F. Sels, Edward I. Solomon, Robert A. Schoonheydt. "Transition-Metal Ions in Zeolites: Coordination and Activation of Oxygen", Inorganic Chemistry, 2010
Crossref 26 words — 1%

- 2 S. Said, D. Aman, M. Riad, S. Mikhail. "MoZn /AlPO4-5 zeolite: Preparation, structural characterization and catalytic dehydration of ethanol", Journal of Solid State Chemistry, 2020
Crossref 23 words — 1%

- 3 Dossi, C.. "On the role of carbonaceous material in the reduction of Cu²⁺ to Cu⁺ in Cu-ZSM-5 catalysts", Applied Catalysis A, General, 19991105
Crossref 19 words — 1%

- 4 repository.stieyapan.ac.id
Internet 19 words — 1%

- 5 Aiguo Wang, Danielle Austin, Abhoy Karmakar, Guy M. Bernard, Vladimir K. Michaelis, Matthew M. Yung, Hongbo Zeng, Hua Song. "Methane Upgrading of Acetic Acid as a Model Compound for a Biomass-Derived Liquid over a Modified Zeolite Catalyst", ACS Catalysis, 2017
Crossref 17 words — < 1%

6 Runduo Zhang, Ning Liu, Zhigang Lei, Biaohua Chen. " Selective Transformation of Various Nitrogen-Containing Exhaust Gases toward N over Zeolite Catalysts ", Chemical Reviews, 2016

17 words — < 1%

Crossref

7 ijeise.upnjatim.ac.id

Internet

17 words — < 1%

8 Chuleehat Sriakkarin, Wasakon Umchoo, Waleeporn Donphai, Yingyot Poo-arporn, Metta Chareonpanich. "Sustainable production of methanol from CO2 over 10Cu-10Fe/ZSM-5 catalyst in a magnetic field-assisted packed bed reactor", Catalysis Today, 2018

16 words — < 1%

Crossref

9 Olivos Suarez, Alma I., Ágnes Szécsényi, Emiel J. M. Hensen, Javier Ruiz-Martínez, Evgeny A Pidko, and Jorge Gascon. "Strategies for the direct catalytic valorization of methane using heterogeneous catalysis: challenges and opportunities", ACS Catalysis

16 words — < 1%

Crossref

10 Yihua Zhang, Ian J. Drake, Alexis T. Bell. "Characterization of Cu-ZSM-5 Prepared by Solid-State Ion Exchange of H-ZSM-5 with CuCl", Chemistry of Materials, 2006

16 words — < 1%

Crossref

11 depositonce.tu-berlin.de

Internet

16 words — < 1%

12 link.springer.com

Internet

16 words — < 1%

13 Aiguo Wang, Danielle Austin, Hui Qian, Hongbo Zeng, Hua Song. "Catalytic Valorization of Furfural

15 words — < 1%

under Methane Environment", ACS Sustainable Chemistry & Engineering, 2018

Crossref

14 Green Chemistry and Sustainable Technology, 2016. 14 words — < 1%

Crossref

15 Soyeon Jeong, Seungdo Yang, Do Heui Kim. "Depolymerization of Protobind lignin to produce monoaromatic compounds over Cu/ZSM-5 catalyst in supercritical ethanol", Molecular Catalysis, 2017 14 words — < 1%

Crossref

16 aip.scitation.org 13 words — < 1%

Internet

17 linknovate.com 13 words — < 1%

Internet

18 www.semanticscholar.org 13 words — < 1%

Internet

19 Millar, G.J.. "Identification of Copper Species Present in Cu-ZSM-5 Catalysts for NO_xReduction", Journal of Catalysis, 19990425 12 words — < 1%

Crossref

20 Xiumei Wang, Jun Xu, Guodong Qi, Bojie Li, Chao Wang, Feng Deng. "Alkylation of Benzene with Methane over ZnZSM-5 Zeolites Studied with Solid-State NMR Spectroscopy", The Journal of Physical Chemistry C, 2013 12 words — < 1%

Crossref

21 pubs.rsc.org 12 words — < 1%

Internet

22 www.liebertpub.com

23 Anderson, S.A.. "Investigation of the effect of carbon monoxide on the oxidative carbonylation of methanol to dimethyl carbonate over Cu⁺X and Cu⁺ZSM-5 zeolites", Journal of Molecular Catalysis. A, Chemical, 20041011
Crossref

24 Peng He, Yingqi Luan, Lulu Zhao, Wei Cheng, Chongchong Wu, Shize Chen, Hua Song. "Catalytic bitumen partial upgrading over Ag-Ga/ZSM-5 under methane environment", Fuel Processing Technology, 2017
Crossref

25 Seung-Kyu Park, Vadim Kurshev, Zhaohua Luan, Chul Wee Lee, Larry Kevan. "Reaction of NO with copper ions in Cu(II)-exchanged ZSM-5 zeolite: electron spin resonance, electron spin echo modulation and Fourier transform infrared spectroscopy", Microporous and Mesoporous Materials, 2000
Crossref

26 Sjovall, H.. "Selective catalytic reduction of NO_x with NH₃ over Cu-ZSM-5-The effect of changing the gas composition", Applied Catalysis B, Environmental, 20060502
Crossref

27 Bahram Ghanbari, Fatemeh Kazemi Zangeneh, Zahra Taheri Rizi, Erfan Aghaei. "High-Impact Promotional Effect of Mo Impregnation on Aluminum-Rich and Alkali-Treated Hierarchical Zeolite Catalysts on Methanol Aromatization", ACS Omega, 2020
Crossref

28 Benjamin E. R. Snyder, Max L. Bols, Robert A. Schoonheydt, Bert F. Sels, Edward I. Solomon. "Iron and Copper Active Sites in Zeolites and Their Correlation to Metalloenzymes", Chemical Reviews, 2017
Crossref 10 words — < 1%

29 Michael J. Manto, Pengfei Xie, Mitchell A. Keller, Wilhelm E. Liano, Tiancheng Pu, Chao Wang. "Recovery of Inorganic Phosphorus Using Copper-Substituted ZSM-5", ACS Sustainable Chemistry & Engineering, 2017
Crossref 10 words — < 1%

30 medialibrary.uantwerpen.be
Internet 10 words — < 1%

31 www.degruyter.com
Internet 10 words — < 1%

32 www.freepatentsonline.com
Internet 10 words — < 1%

33 www.linknovate.com
Internet 10 words — < 1%

34 www.tandfonline.com
Internet 10 words — < 1%

35 Alessandro Longo, Stavros Alexandros Theofanidis, Chiara Cavallari, Nadadur Veeraraghavan Srinath et al. "What Makes Fe-Modified MgAl O an Active Catalyst Support? Insight from X-ray Raman Scattering ", ACS Catalysis, 2020
Crossref 9 words — < 1%

36 Haixia Wu, Jiawei Fan, Yongjun Sun, Ruoyu Liu, Juncheng Jin, Pengcheng Li. "Removal of ammonia nitrogen and phenol by pulsed discharge plasma combined 9 words — < 1%

with modified zeolite catalyst", Journal of Environmental Management, 2021

Crossref

37 Le Yang, Jinxu Huang, Rui Ma, Rui You, Hui Zeng, Zebao Rui. " Metal–Organic Framework-Derived IrO /CuO Catalyst for Selective Oxidation of Methane to Methanol ", ACS Energy Letters, 2019

Crossref

38 Snehasish Mishra, Puneet Kumar Singh, Pratikhya Mohanty, Tapan Kumar Adhya et al. "Green synthesis of biomethanol—managing food waste for carbon footprint and bioeconomy", Biomass Conversion and Biorefinery, 2022

Crossref

39 coek.info

Internet

40 ebin.pub

Internet

41 kuscholarworks.ku.edu

Internet

42 mediatum.ub.tum.de

Internet

43 onlinelibrary.wiley.com

Internet

44 www.mdpi.com

Internet

45 www.sphinxesai.com

Internet

46 A.V Salker, W Weisweiler. "Catalytic behaviour of metal based ZSM-5 catalysts for NO_x reduction with NH₃ in dry and humid conditions", Applied Catalysis A: General, 2000 8 words — < 1%

Crossref

47 Alexander A. Kolganov, Anton A. Gabrienko, Svetlana A. Yashnik, Evgeny A. Pidko, Alexander G. Stepanov. "Nature of the Surface Intermediates Formed from Methane on Cu-ZSM-5 Zeolite: A Combined Solid-State Nuclear Magnetic Resonance and Density Functional Theory Study", The Journal of Physical Chemistry C, 2020 8 words — < 1%

Crossref

48 Divakar, D.. "Catalytic oxidation of trichloroethylene over Fe-zeolites", Catalysis Today, 20111101 8 words — < 1%

Crossref

49 Eelco T.C. Vogt, Gareth T. Whiting, Abhishek Dutta Chowdhury, Bert M. Weckhuysen. "Zeolites and Zeotypes for Oil and Gas Conversion", Elsevier BV, 2015 8 words — < 1%

Crossref

50 Kamel Shoueir, Saleh Kandil, Hamza El-hosainy, Maged El-Kemary. "Tailoring the surface reactivity of plasmonic Au@TiO₂ photocatalyst bio-based chitosan fiber towards cleaner of harmful water pollutants under visible-light irradiation", Journal of Cleaner Production, 2019 8 words — < 1%

Crossref

51 Kyung Soo Park, Jeong Hwa Kim, So Hyun Park, Dong Ju Moon et al. "Direct activation of CH₄ to oxygenates and unsaturated hydrocarbons using N₂O on Fe-modified zeolites", Journal of Molecular Catalysis A: Chemical, 2017 8 words — < 1%

Crossref

52 Qi, G.. "Ultra-active Fe/ZSM-5 catalyst for selective catalytic reduction of nitric oxide with ammonia", Applied Catalysis B, Environmental, 20050901 8 words — < 1%
Crossref

53 Sriatun, Heru Susanto, Widayat, Adi Darmawan. "Characteristic of ZSM-5 catalyst supported by nickel and molybdenum", IOP Conference Series: Materials Science and Engineering, 2019 8 words — < 1%
Crossref

54 Vincent Blay, Benoît Louis, Rubén Miravalles, Toshiyuki Yokoi, Ken A. Peccatiello, Melissa Clough, Bilge Yilmaz. "Engineering Zeolites for Catalytic Cracking to Light Olefins", ACS Catalysis, 2017 8 words — < 1%
Crossref

55 Xiaocui Wei, Xiangfei Xue, Liu Wu, Haozhe Yu, Jie Liang, Yifei Sun. "High-grade bio-oil produced from coconut shell: A comparative study of microwave reactor and core-shell catalyst", Energy, 2020 8 words — < 1%
Crossref

56 Xiaoju Cui, Rui Huang, Dehui Deng. "Catalytic conversion of C1 molecules under mild conditions", EnergyChem, 2021 8 words — < 1%
Crossref

57 Xueting Wang, Adam A. Arvidsson, Magdalena O. Cichocka, Xiaodong Zou et al. "Methanol Desorption from Cu-ZSM-5 Studied by Infrared Spectroscopy and First-Principles Calculations", The Journal of Physical Chemistry C, 2017 8 words — < 1%
Crossref

58 docecity.com 8 words — < 1%
Internet

-
- 59 repositorio.unicamp.br Internet 8 words — < 1%
-
- 60 research.chalmers.se Internet 8 words — < 1%
-
- 61 revistavalore.emnuvens.com.br Internet 8 words — < 1%
-
- 62 www.frontiersin.org Internet 8 words — < 1%
-
- 63 www.nature.com Internet 8 words — < 1%
-
- 64 Mohammed C. Al-Kinany, Saeed M. Alshihri, Saud A. Aldrees, Eyad A. Alghilan et al. "chapter 1 Catalysis in Alkylation of Benzene With Ethene and Propene to Produce Ethylbenzene and Isopropylbenzene", IGI Global, 2020 Crossref 7 words — < 1%
-
- 65 Silvia Bordiga, Elena Groppo, Giovanni Agostini, Jeroen A. van Bokhoven, Carlo Lamberti. "Reactivity of Surface Species in Heterogeneous Catalysts Probed by In Situ X-ray Absorption Techniques", Chemical Reviews, 2013 Crossref 7 words — < 1%
-
- 66 M. Haris Mahyuddin, Aleksandar Staykov, Yoshihito Shiotā, Mayuko Miyanishi, Kazunari Yoshizawa. " Roles of Zeolite Confinement and Cu-O-Cu Angle on the Direct Conversion of Methane to Methanol by [Cu (μ-O)] -Exchanged AEI, CHA, AFX, and MFI Zeolites ", ACS Catalysis, 2017 Crossref 6 words — < 1%

67 Navlani-García, M., B. Puértolas, D. Lozano-Castelló, D. Cazorla-Amorós, M. V. Navarro, and T. García. "CuH-ZSM-5 as Hydrocarbon Trap under Cold Start Conditions", Environmental Science & Technology, 2013. 6 words — < 1%
Crossref

68 Villa, A.L.. "Cu- and Fe-ZSM-5 as catalysts for phenol hydroxylation", Journal of Molecular Catalysis. A, Chemical, 20050316 6 words — < 1%
Crossref

EXCLUDE QUOTES ON

EXCLUDE SOURCES OFF

EXCLUDE BIBLIOGRAPHY ON

EXCLUDE MATCHES OFF