International Journal of Technology 14(1) 142-151 (2023)
Received April 2021 / Revised May 2021 / Accepted August 2021

International Journal of Technology

http://ijtech.eng.ui.ac.id

Improvement of Catalyst Activity in Methanol-to-Olefin Conversion via Metal (Sr/La) Impregnation over ZSM-5 Catalyst

Heri Heriyanto[1,2], Oki Muraza[3], Galal A. Nasser[4], Mohammed Ahmed Sanhoob[4], Idris A. Bakare[4], Budhijanto[1], Rochmadi[1], Karna Wijaya[5], Arief Budiman[1*]

[1]*Chemical Engineering Department, Universitas Gadjah Mada, Jalan Grafika 2, Yogyakarta 55281, Indonesia*
[2]*Chemical Engineering Department, University of Sultan Ageng Tirtayasa, Cilegon, 42435, Indonesia*
[3]*Research & Technology Innovation, Pertamina, Sopo Del Building, 51st Fl. Jl. Mega Kuningan Barat III, Jakarta Pusat, 12950, Indonesia*
[4]*Center of Excellence in Nanotechnology (CENT) and Chemical Engineering Department, King Fahd University of Petroleum and Minerals, Dhahran, 31261, Saudi Arabia*
[5]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Yogyakarta, 55281, Indonesia*

Abstract. The use of methanol over ZSM-5 and modified catalysts for the production of light olefins has emerged as an effective new strategy for this industry. In the methanol-to-olefin (MTO) process, the challenges are maintaining product selectivity and prolonging the lifetime of the catalyst catalyst manufacturing become. The effect of strontium (Sr) and lanthanum (La) impregnated over the ZSM-5 catalyst on MTO conversion was investigated in this study. The results showed that the metals impregnated on ZSM-5 had influenced its acidity strength and improved catalyst activity and lifetime in the MTO process. When a metal strontium of 5 wt.% was impregnated, the quantity of Bronsted acid sites (BAS) in the parent ZSM-5 was reduced to 81.53%. The catalyst 5La-ZSM-5 modified improved the selectivity of light olefin ca. 88% and high conversion methanol 100% for 15 h time-on-stream. The sequence of catalyst activity was 5La-ZSM-5 > 3La-ZSM-5 > 5Sr-ZSM-5 > 3Sr-ZSM-5 > parent-ZSM-5. The role of metal (Sr/La) impregnated over ZSM-5 is important for reducing acidity and prolonging activity catalyst from 7 to 14 h.

Keywords: Catalyst lifetime; Impregnated; Lanthanum; Olefin; Strontium

1. Introduction

To produce polymeric materials and other products, the plastics industry depends on light olefins ($\boldsymbol{C_2^=}, \boldsymbol{C_3^=}, \boldsymbol{C_4^=}$), which are obtained mostly from petroleum and naphtha (Gao *et al.*, 2018). The demand for olefins increases, while the feedstocks of naphtha and petroleum are limited and non-renewable, thus requiring the development of prolonging alternative routes for new olefin production technologies from non-petroleum and renewable resources (Pugazhendhi *et al.*, 2020; Ahmadpour and Taghizadeh, 2016; Jamil *et al.*, 2014). Moreover, the overuse of petroleum for industrial purposes has increased environmental issues, such as greenhouse gasses emissions, air pollution, and climate change, due to the increase in CO_2 in the atmosphere (Sudibandriyo and Putri, 2020; Aziz *et al.*, 2019). In recent years, scientists have comprehensively studied and developed the technology to

*Corresponding author's email: abudiman@ugm.ac.id, Tel.: +62-274-555320
doi: 10.14716/ijtech.v14i1.4884

produce olefins via methanol (which can be sourced from renewable materials) to resolve the crisis of feedstock of petroleum and naphtha and the environmental damage due to global warming from CO_2 (Barnwal and Sharma, 2005).

The research for the development of the MTO process would focus on the modification of catalysts to increase light olefin selectivity (especially C_2 and C_3), determine detailed reaction mechanisms in the formation of olefins, and increase catalyst lifetime for the MTO process. The MTO process often uses ZSM-5 as a catalyst (Gorzin *et al.*, 2019). However, the presence of strong acid sites on the ZSM-5 catalyst leads to the formation of coke and eventually deactivates the catalyst (Chen *et al.*, 2017; Zhang *et al.*, 2012). For this reason, several scientists have carried out studies and developed strategies to enhance the activity of the catalyst, product distribution, and address the deactivation of the catalyst in the MTO process. Some of the strategies in the development of ZSM-5 include adjusting its acidity (Yaripour *et al.*, 2015; Liu *et al.*, 2009), morphology and size (Chen *et al.*, 2017), and synthesis of hierarchical pore structure (Li *et al.*, 2020; Gorzin *et al.*, 2019; Rostamizadeh, Yaripour, and Hazrati 2018; Ahmadpour and Taghizadeh, 2016). According to Li *et al.*, once the metal (Zr) was impregnated with the acid, the acid's strength decreased, and its treatment increased the catalyst's activity (Li *et al.*, 2020).

Reducing catalyst deactivation and increasing the selectivity to olefins are still imminent problems in the MTO process. Based on that, this research evaluated the effect of Sr and La metals impregnated over ZSM-5 in the MTO process. The ZSM-5 catalyst employed during this study contains 30 wt.% pseudo-boehmite. In addition, few authors have mentioned utilizing pseudo-boehmite as a binder in combination with ZSM-5. The binder's functions on the ZSM-5 catalyst are as follows: improved mechanical and thermal stability and internal bonding between pores; protection of the catalyst from inert material that would block its pores; and enhanced porosity and mass transfer. In addition, the acidity of catalyst is crucial for the MTO process. Since the parent ZSM-5 has highly acidic sites, the hydrogen transfer reaction is facilitated, and hence paraffin is formed. Furthermore, the strong acid sites also facilitated the fast deactivation of the active sites. Hence, we impregnated Sr and La over the ZSM-5 catalyst to modify the acidity of active sites to achieve a more active and stable catalyst system.

2. Methods

2.1. Materials and Sample Preparation

The ZSM-5 Catalyst was obtained from ACS material LCC catalyst with CAS No. 1318-02-1, while strontium with CAS No. 7440-24-6, methanol with CAS No. 67-56-1, and Lanthanum CAS with No. 10277-43-7 from Sigma Aldrich, respectively. In accordance with previous research, Bakare *et al.* (2018) reported that all modified catalysts were synthesized using an impregnation method. About 7 g of ZSM-5 catalyst was dissolved in 10 ml of deionized water and agitated at 200 rpm for ten minutes. Afterward, metal (Sr/La) equivalent to 3 - 5 wt.% was added into the solution and agitated at 200 rpm until a homogeneous mixture is formed. Thereafter, the products were dried at 70 °C overnight and then calcined at 600 °C for 5 h at a heating rate 5 ^{0}C/h. The impregnated samples were labelled as XA-ZSM-5 (where 'A' the amount of metal in wt.% = 3 or 5 and 'X' represents the metal la or Sr). Hence, the authors have the following samples: 3Sr-ZSM-5; 5Sr-ZSM-5; 3La-ZSM-5, and 5La-ZSM-5.

2.2. Characterization

To gain a deeper understanding of the properties of ZSM-5 catalyst systems, their characterization before and after modification was comprehensively investigated. The

crystallinity and bulk phase of all samples were examined using X-Ray Diffraction (XRD). X-Ray Diffraction (XRD) was utilized to examine the crystallinity and bulk phase of all samples. SEM-EDX (FE-SEM, LYRA 3 Dual Beam, Tescan, and EDX, Oxford Instruments) was used to look at the surface topography of the catalyst and see if there were any Sr or La-impregnated samples. As a probe molecule, pyridine was used to determine the number of Bronsted acidity sites and Lewis acid sites. The acidity of a catalyst is proportional to the number of pyridine molecules adsorbed at the acid site. The pyridine adsorption experiment was conducted on a Nicolet 6700 FTIR spectrometer. In a typical analysis, the sample is pressed into a wafer (50mg) and placed into a high-temperature pressure heating cell, which is continuously evacuated. The sample is then calcined at 500 ^{0}C for 3 minutes and then cooled down to 150 ^{0}C. Bare catalyst spectra are then recorded prior to pyridine adsorption. Following pyridine adsorption, the sample is then evacuated for 30 minutes and the IR spectra are then collected. Finally, the IR spectra of the untreated parent sample are subtracted from those of the pyridine-treated sample. Equation 1 is then used to calculate the number of acid sites based on the integration of peak area for both Bronsted and Lewis acid sites.

$$C_B = \frac{A\ x\ S_B}{\varepsilon_B\ x\ w} \quad (1)$$

In this case C_B, A, w, SB, ε_B represent the concentration Bronsted acid (mmol/g), area of sample (cm^2), weight of catalyst (mg), constant od Bronsted acid, and the area of integration of the FTIR pyridine analysis results curve for the BAS.

The nitrogen physisorption properties of synthesized catalysts were carried out on an ASAP 2020 (Micromeritics). The surface area of the catalyst systems was then calculated using the BET model. In addition, Figure 1 depicts the schematic diagram for evaluating catalyst systems.

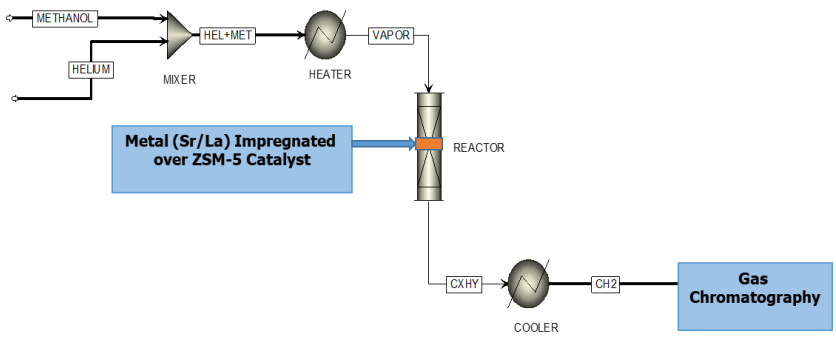


Figure 1 The schematic diagram for the preparation of the catalyst and test performance

2.3. Catalytic Reactions

The Micro Activity Test (MAT) has been done in a plug flow reactor to observe the activity of the modified catalyst in the MTO process. Metal-modified ZSM-5 zeolites were analyzed in the MTO process (Me-ZSM-5) at 500°C, 1 bar, and WHSV 4.5 h-1on an automated Computerized PID Microactivity-Effi (DUO/TWIN/PARALLEL) catalytic reactor. The reactor unit is equipped with an online GC product analysis. In a typical run, 0.1 mg of catalyst was charged to the reactor and the flow rate of methanol and gas helium were maintained at 0.01 mL/minute, and 18.60 mL/minute, respectively. The conversion and selectivity of each product were calculated by equations 2 and 3, respectively:

$$C_{CH_3OH} = \frac{n\,(CH_3OH)_{in} - n\,(CH_3OH)_{out} - 2n\,(C_2H_5O)_{out}}{n\,(CH_3OH)_{in}}\ x\ 100\ \% \quad (2)$$

$$S_{C_xH_y} = \frac{X\ x\ (C_xH_y)_{out}}{n\,(CH_3OH)_{in} - n\,(CH_3OH)_{out} - 2n\,(C_2H_5O)_{out}}\ x\ 100\ \% \quad (3)$$

Where C_{CH3OH} represents methanol and C_2H_5O represents DME. $(C_xH_y)_{out}$ is the concentration of any hydrocarbon in the effluent product such as DME and targeted product (such as ethylene, propylene, butylene, etc.). C_{CH3OH} subscripted aim to conversion methanol and $S_{C_xH_y}$ subscripted aim to the selectivity of hydrocarbon.

3. Results and Discussion

3.1. Effect of Metal (Sr/La) Impregnated on Relative Crystallinity of Catalyst

The effect of metals (Sr/La) impregnation on the structural patterns and peak intensity over ZSM-5 catalyst has been investigated using XRD as presented in Figure 2.

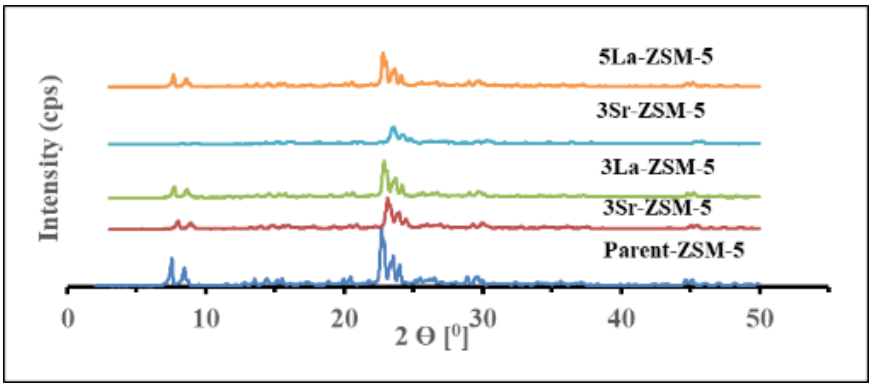


Figure 2 XRD patterns of parent and impregnations ZSM-5 with Sr and La metals samples: 3 – 5 wt. %

The results show that all samples impregnated with Sr and La (3 - 5 wt.%) have the same peak pattern as parent ZSM-5 zeolite although with lower peak intensities as an indicator for metal impregnation. However, the metals impregnated on the parent ZSM-5 catalyst did not affect the diffraction peaks of the parent catalyst. Also, there is no XRD pattern which indicates the presence of metal and impurity. These phenomena showed that the content of metals (Sr and La) was x-ray amorphous and the metal is dispersed on the surface causing no significant changes to its structure. The experimental results by Li *et al.* are consistent with this finding (Li, Rezaei, and Rownaghi, 2019). According to their results, the impregnation of m Ga/La/Mg/Y on ZSM-5 had no significant effect on the observed peaks and the absence of additional peaks indicates that these metals are well dispersed on ZSM-5 zeolite.

3.2. Effect of Metal (Sr/La) Impregnated on the Catalyst Composition of ZSM-5

Figure 3 shows the findings of a Scanning Electron Microscopy - EDX investigation of the surface morphology of the sample before and after modification with metal (Sr/La). The results illustrated that the before and after modified catalysts have the same morphological shape, which is hexagonal with non-sharp angles. Furthermore, the SEM analysis of ZSM-5 modified with La shows aggregated hexagonal crystals without sharp angles, while Sr modified a wider hexagonal morphology as shown in Figure 3. Generally, there are no clear differences in the morphological properties of the samples prepared. The uniformity and regularity of crystalline morphology would provide a good pathway to the active site and may affect the selectivity of hydrocarbon in the MTO process.

In addition, the elemental composition of Sr and La metals impregnated over the parent ZSM-5 catalyst is as presented in Table 1. Based on the analysis, the Si / Al ratio increases after impregnating Sr and La metals. This might be due to the decrease in element Al over the ZSM-5 catalyst via dealumination.

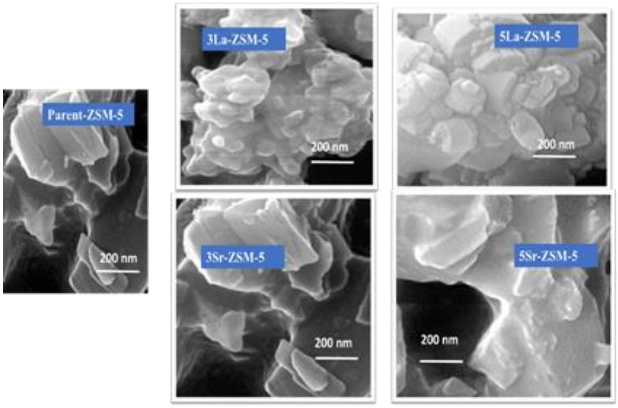


Figure 3 SEM – EDX metal (Sr/La) impregnation at 3 wt.% and 5 wt.% concentrations

Table 1 EDX analysis of parent and modified ZSM-5

Sample	Composition [wt. %]								
	Si	Al	O	Mg	Ca	Ba	La	Sr	Si/Al
ZSM-5	40.40	2.70	57.50	-	-	-	-	-	14.96
3Sr-ZSM-5	47.35	2.20	45.78	-	-	-	-	4.68	21.52
3La-ZSM-5	38.68	1.92	55.61	-	-	-	3.79	-	19.10
5Sr-ZSM-5	35.37	1.76	58.74	-	-	-	-	4.12	20.09
5La-ZSM-5	40.34	1.88	53.45	-	-	-	4.32	-	21.46

3.3. Effect of Metal (Sr/La) Impregnated on Catalyst Acidity

The acidity analysis of the prepared catalyst systems was carried out with pyridine as a probe molecule. Figure 4 illustrates the Adsorption bands of absorbed pyridine (1700-1400 cm^{-1}).

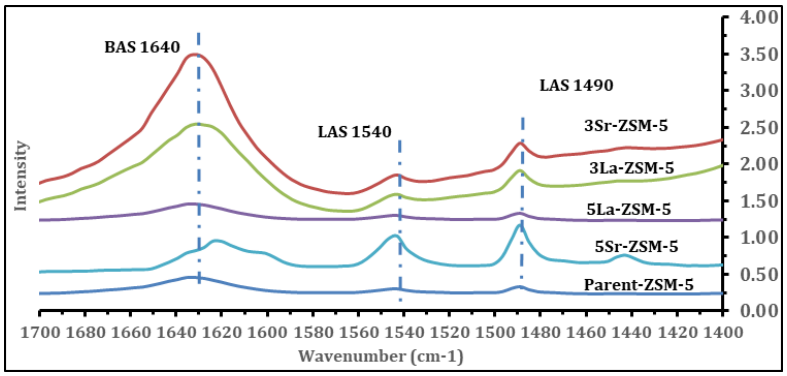


Figure 4 Pyridine FT-IR spectra of parent-ZSM-5, 3wt.% and 5 wt.% Sr, and La metal modified ZSM-5

In Figure 4, the absorption spectrum band at a wave number around 1490 cm^{-1} shows the Lewis acid sites. Moreover, the absorption band at a wave number around 1630 cm^{-1} shows the Brønsted acid sites. The increase in the intensities of absorption peaks indicates the induction of more weak and medium acid sites in both 3Sr-ZSM-5 and 3La-ZSM-5 catalysts. The extent of the increased absorption peak relates to the amount of weak and medium acid sites formed on both catalysts (Bakare *et al.*, 2016). In addition, the acidity

analysis of the catalyst before and after modification with metal (Sr/La) impregnated is presented in Table 2.

Table 2 The acidity of parent and Me-ZSM-5

Sample	Acid amount (mmol g^{-1})		
	BAS	LAS	TOTAL
Parent-ZSM-5	0.773	0.014	0.787
3Sr-ZSM5	0.673	0.007	0.680
3La-ZSM5	0.689	0.006	0.695
5Sr-ZSM5	0.143	0.002	0.149
5La-ZSM5	0.195	0.001	0.196

As demonstrated in Figure 4, the amount of Bronsted acid sites and Lewis acid sites was calculated quantitatively by integrating the area below the peak spectra. The Bronsted and Lewis acid sites were then calculated based on Eq. 1. The analysis concluded that metal impregnation on ZSM-5 could reduce the Bronsted acid site catalyst. This is because the La^{2+} and Sr^{2+} cations impregnated would react with the H^{+} protons in the parent ZSM-5 catalyst, so the content of protons decreases. Bronsted acid site was detected due to the reaction of the pyridine substance with protons on the surface catalyst and Pyridium ions were formed. Because the content of protons in ZSM-5 modified catalyst decreased due to interaction with La^{2+} and Sr^{2+} cations, as a result, the Bronsted acid site is decreased.

3.4. Effect of Metal (Sr/La) Impregnated on N_2 Adsorption analysis

The surface area and cavity size are properties necessary in the characterization of a solid acid catalyst. The physisorption analysis of isothermal adsorption-desorption nitrogen of all catalyst systems is presented in Figure 5.

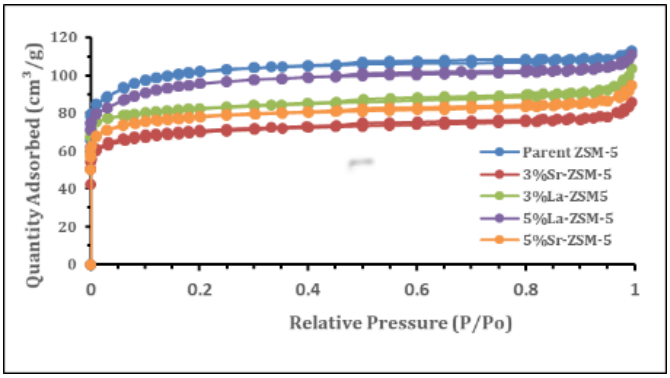


Figure 5 N_2 adsorption/desorption isotherms of the parent ZSM-5 and impregnation with Sr and La metals: 3 – 5 wt.%

According to Figure 5, the isotherms showed a type IV isotherm pattern with peculiar mesoporous materials characterized by hysteresis loops. In line with the findings of Chin *et al.* (2019), the catalyst type IV isotherm exhibits a hysteresis loop. Table 3 displays the surface area of the samples before and after impregnation.

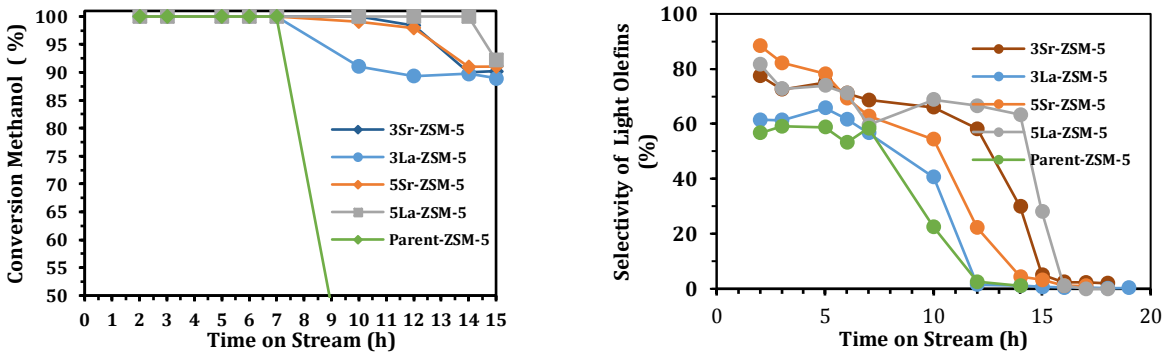
Table 3 Complete result of N_2 adsorption analysis.

Sample	S_{BET} (m^2/g)	S_{EXT} (m^2/g)	S_{Micro} (m^2/g)	V_T (cm^3/g)	V_{Micro} (cm^3/g)
H-ZSM-5	377	99	278	0.17	0.11
3%La-ZSM-5	307	49	257	0.15	0.11
5%La-ZSM-5	353	101	251	0.16	0.11
3%Sr-ZSM-5	262	57	204	0.12	0.08
5%Sr-ZSM-5	292	57	237	0.14	0.10

The data shows that after the metal impregnation, the BET surface area decreased from ca. 377 m^2/g to the smallest area of ca. 262 m^2/g (in 3Sr-ZSM-5). The sequence of surface area from highest to lowest is parent ZSM5 > 5La-ZSM-5 > 3La-ZSM-5 > 5Sr-ZSM-5 > 3Sr-ZSM-5. The result shows that the surface area for 5% loading for both metals is higher than 3%. These phenomena describe how the impregnated metal was distributed relatively even to all surfaces. Furthermore, the adhesion interaction between the metal and the surface of the zeolite is relatively stronger, so there is no accumulation in the mouth and pore channels. In addition, the contributory effect of dealumination as observed from EDX analysis might be an indicator for the cause of this anomaly. Moreover, decreasing total pore volume indicated that metal-impregnated on ZSM-5 tends to block the pores. In addition, the atomic radius in lanthanum > strontium which is 2.5 ^{0}A> 2.0 ^{0}A, respectively. Hence, the smaller strontium metal could migrate more into the zeolite pore and cause more decrease in the pore volume of the resulting catalyst. After that, the absorption data showed that the microporous volume (0.11 cm3/g) was preserved in both the parent and modified ZSM-5, resulting in minimal changes to the microporous area, as shown in Table 3. Thus, the impregnated metals were mainly deposited on the surface and mesopores of the catalyst, causing a decrease in the surface area and mesoporous.

3.5. Micro Activity Test (MAT)

The performance test of the ZSM-5 catalyst before and after modification for MTO reaction was observed in the plug flow reactor with parameters process at 500 ^{0}C, 1 bar, and WHSV 4.5 hr^{-1}. All sample catalyst explains the high conversion of methanol to hydrocarbons (100 %) for a long time. The methanol conversion and selectivity light olefin function TOS are presented in Figure 6.



(a) (b)

Figure 6 Effect of metal (Sr/La) impregnated 3 -5 wt.% over ZSM-5 catalyst (a) on the conversion as a function of time on stream (TOS); (b) selectivity of light olefin

Figure (6a) showed that the conversion of the parent ZSM-5 catalyst decreased after 7 h time on stream from 100 to 70 %. This decrease is due to the onset of deactivation by coking on the parent catalyst, hence methanol is no longer converted to targeted hydrocarbons. When it came to methanol conversion, the 5La-ZSM-5 showed the best performance, maintaining a constant 100% conversion for up to 15 hours on stream. The order of catalyst activity is 5La-ZSM-5 > 3La-ZSM-5 > 5Sr-ZSM-5 > 3Sr-ZSM-5 > parent-ZSM-5. The concentration of metal impregnated over the ZSM-5 catalyst influenced the activity of catalyst for methanol conversion. This result was in line with Heriyanto *et al.* (2020) and where the impregnated metal (Ca) causes the activity of the catalyst to increase. In addition, at higher metal concentrations, the metal impregnated would be more distributed on the catalyst than the low concentration. Hence, the active sites increase, and the activity of the catalyst increases. strontium is an alkaline earth metal and lanthanum is a transition metal

with a valence of 2^+ (divalent) and 3^+ (trivalent), respectively. The covalent radius of strontium higher than lanthanum are 1.82 Å and 1.94 Å, respectively. The exchange of Sr^{2+} and La^{3+} cations with H^+ from ZSM-5 causes a decrease in the BAS and increases the LAS (Khezri *et al.*, 2020).

The total acid strength of ZSM-5 decreases with Sr^{2+} and La^{2+} cation elements because LAS are generally weaker in line with BAS in zeolites. The parent ZSM-5 catalyst achieved a light olefin selectivity of 53.19%, which decreased after 7 hours. Meanwhile, the 5Sr-ZSM-5 catalyst was able to achieve the highest light olefin selectivity, which reached 88.38%. Nevertheless, this value begins to decrease after 7 hours have passed. The sequence of catalyst lifetime is 5La-ZSM-5> 3Sr-ZSM-5> 5Sr-ZSM-5> 3La-ZM-5> parent-ZSM-5. Finally, increasing selectivity of light olefin correlated with a decrease in the acid strength of the catalyst acid sites. Additionally, Figure 7 illustrates the influence of metal (Sr/La) impregnated over ZSM-5 on product distribution.

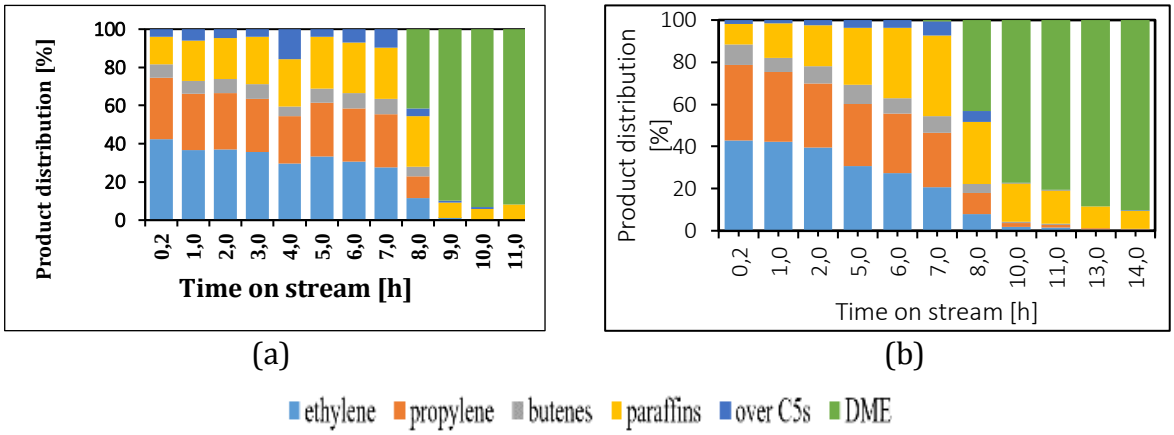


Figure 7 Effect of metal impregnated on product distribution MTO process (a) 5Sr-ZSM-5 and (b) 5La-ZSM-5

The olefin selectivity on Sr-ZSM-5 is higher than La-ZSM-5, which is 78% and 69.86%, respectively. This result is consistent with the findings of Sudibandriyo and Putri (2020), who reported that pore diameter and surface area influenced the selectivity product. In addition, this could be related to the acidity of catalyst systems. The impregnation of strontium caused the Bronsted Acid Site to decrease to 12.82 % (assuming that the parent BAS is 100 percent). This result is in line with a report from Jamilatun *et al.* (2019) product composition was influenced type of catalyst. The lower acidity would prevent the hydrogen transfer and the formation of paraffin and cokes decreases. Consequently, the product selectivity of olefin and lifetime catalyst increases. Furthermore, at the 6^{th} hour, DME is produced via methanol dehydration in a catalytic fixed-bed reactor (Wahid and Utomo, 2019). DME was formed as the selectivity to olefin decreased. Subsequently, the selectivity to DME dominates the product distribution. As shown in Table 2, the appearance of DME is due to a decrease in the number of acid sites on the surface. The results indicate that the dehydration of methanol to DME is a function of external surface area, the number of strong acid sites, crystal size, and reaction temperature. The following is the proposed mechanism reaction on the MTO process:

$$2\,CH_3OH \overset{K1}{\Leftrightarrow} CH_3OCH_3 + H_2O \quad (4)$$

$$2\,CH_3OCH_3 \overset{k_2}{\rightarrow} C_2H_4 + 2CH_3OH \quad (5)$$

$$2CH_3OH \overset{k_3}{\rightarrow} C_2H_4 + 2H_2O \quad (6)$$

$$C_2H_4 + CH_3OCH_3 \overset{k_4}{\rightarrow} CH_3OH + C_3H_6 \quad (7)$$

4. Conclusions

The impregnation of Sr and La metals positively affected the ZSM-5 parent's activity and lifetime. The Bronsted acid site of parent ZSM-5 decreases until 81.53% when strontium of 5 wt. % was impregnated. Sr^{2+} cations impregnated substituted H^+ protons in the parent ZSM-5 catalyst, so the content of H^+ protons over parent ZSM-5 decreases. Reducing acidity would prevent hydrogen transfer, increase olefin selectivity, and reduce coke formation, hence resulting in an increased catalyst lifetime. 5La-ZSM-5 catalyst improved the selectivity of light olefin c.a. 88 % and presented high conversion of methanol 100% for 15 h time on stream. The order of catalyst activity is 5La-ZSM-5 > 3La-ZSM-5 > 5Sr-ZSM-5 > 3Sr-ZSM-5 > parent-ZSM-5. The authors suggest extensive research into the effect of crystal size, mesoporosity, and acid site distribution on the catalytic performance in selective methanol conversion to olefin.

Acknowledgments

The authors express gratitude to the Ministry of Research and Technology/National Agency for Research and Innovation of the Republic of Indonesia for research funding (Contract no: 170/SP2H/AMD/LT/DRPM/2020), the Ministry of Finance of the Republic of Indonesia (LPDP) for the Doctoral Program Scholarship, and the Center of Excellence Nano Technology (CENT) - King Fahd University of Petroleum and Minerals - Saudi Arabia for supporting research facilities.

References

Ahmadpour, J., Taghizadeh, M., 2016. One-pot synthesis of hierarchically mesoporous zsm-5 using different combinations of mesogenous templates. *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry,* Volume 46(8), pp. 1133–1141

Aziz, M.A.A., Setiabudi, H.D., Teh, L.P., Annuar, N.H.R., Jalil, A.A., 2019. A review of heterogeneous catalysts for syngas production via dry reforming. *Journal of the Taiwan Institute of Chemical Engineers,* Volume 101, pp. 139–158

Bakare, I.A., Muraza, O., Sanhoob, M.A., Miyake, K., Hirota, Y., Yamani, Z.H., Nishiyama, N., 2018. Dimethyl ether-to-olefins over aluminum rich ZSM-5: The role of Ca and La as modifiers. *Fuel,* Volume 211, pp. 18–26

Bakare, I.A., Muraza, O., Yoshioka, M., Yamani, Z.H., Yokoi, T., 2016. Conversion of methanol to olefins over Al-rich ZSM-5 modified with alkaline earth metal oxides. *Catalysis Science & Technology,* Volume 6(21), pp. 7852–7859

Barnwal, B.K., Sharma, M.P., 2005. Prospects of biodiesel production from vegetable oils in India. R*enewable and Sustainable Energy Reviews*, Volume 9(4), pp. 363–378

Chen, H., Wang, Y., Meng, F., Sun, C., Li, H., Wang, Z., Gao, F., Wang, X., Wang, S., 2017. Aggregates of superfine ZSM-5 crystals: The effect of NaOH on the catalytic performance of methanol to propylene reaction. *Microporous and Mesoporous Materials,* Volume 244, pp. 301–309

Chin, K.C., Leong, L.K., Lu, S.Y., Tsai, D.H., Sethupathi, S., 2019. Preparation of metal organic framework (mof) derived bimetallic catalyst for dry reforming of methane. *International Journal of Technology*, Volume 10, p. 1437

Gao, P., Xu, J., Qi, G., Wang, C., Wang, Q., Zhao, Y., Zhang, Y., Feng, N., Zhao, X., Li, J., Deng, F., 2018. A mechanistic study of methanol-to-aromatics reaction over ga-modified zsm-5 zeolites: understanding the dehydrogenation process. *ACS Catalysis*, Volume 8(10), pp. 9809–9820

Gorzin, F., Darian, J.T., Yaripour, F., Mousavi, S.M., 2019. Synthesis of highly crystalline nanosized HZSM-5 catalyst employing combined hydrothermal and sonochemical method: Investigation of ultrasonic parameters on Physico-chemical and catalytic performance in methanol to propylene reaction. *Journal of Solid State Chemistry*, Volume 271, pp. 8–22

Heriyanto, H., Muraza, O., Nasser, G.A., Sanhoob, M.A., Bakare, I.A., Budhijanto, Rochmadi, Budiman, A., 2020. Development of new kinetic models for methanol to hydrocarbons over a Ca-ZSM-5 catalyst. *Energy & Fuels,* Volume 34(5), pp. 6245–6260

Jamil, A.K., Muraza, O., Yoshioka, M., Al-Amer, A.M., Yamani, Z.H., Yokoi, T., 2014. Selective production of propylene from methanol conversion over nanosized zsm-22 zeolites. *Industrial & Engineering Chemistry Research,* Volume 53(50), pp. 19498–19505

Jamilatun, S., budhijanto, B., Rochmadi, R., Yuliestyan, A., Budiman, A., 2019. Effect of grain size, temperature and catalyst amount on pyrolysis products of Spirulina Platensis Residue (SPR). *International Journal of Technology*, Volume 10(3), pp. 541–550

Khezri, H., Izadbakhsh, A., Izadpanah, A.A., 2020. Promotion of the performance of La, Ce and Ca-impregnated HZSM-5 nanoparticles in the MTO reaction. *Fuel Processing Technology,* Volume 199, p 106253

Li, D., Xing, B., Wang, B., Li, R., 2020. Activity and selectivity of methanol-to-olefin conversion over Zr-modified H-SAPO-34/H-ZSM-5 zeolites - A theoretical study. *Fuel Processing Technology,* Volume 199, p. 106302

Li, X., Rezaei, F., Rownaghi, A.A., 2019. Methanol-to-olefin conversion on 3D-printed ZSM-5 monolith catalysts: Effects of metal doping, mesoporosity, and acid strength. *Microporous and Mesoporous Materials,* Volume 276, pp. 1–12

Liu, J., Zhang, C., Shen, Z., Hua, W., Tang, Y., Shen, W., Yue, Y., Xu, H., 2009. Methanol to propylene: Effect of phosphorus on a high silica HZSM-5 catalyst. *Catalysis Communications*, Volume 10(11), pp. 1506–1509

Pugazhendhi, A., Alagumalai, A., Mathimani, T., Atabani, A.E., 2020. Optimization, kinetic and thermodynamic studies on sustainable biodiesel production from waste cooking oil: An Indian perspective. *Fuel,* Volume 273, p. 117725

Rostamizadeh, M., Yaripour, F., Hazrati, H., 2018. High efficient mesoporous HZSM-5 nanocatalyst development through desilication with a mixed alkaline solution for methanol to olefin reaction. *Journal of Porous Materials*, Volume 25(5), pp. 1287–1299

Sudibandriyo, M., Putri, F.A., 2020. The effect of various zeolites as an adsorbent for bioethanol purification using a fixed bed adsorption column. *International Journal of Technology*, Volume 11(7), pp. 1300–1308

Wahid, A., Utomo, W.R., 2019. Application of multivariable model predictive control (4x4) for dimethyl ether purification from methanol. *International Journal of Technology*, Volume 10(6), pp. 1211–1219

Yaripour, F., Shariatinia, Z., Sahebdelfar, S., Irandoukht, A., 2015. Effect of boron incorporation on the structure, product selectivities, and a lifetime of H-ZSM-5 nanocatalyst designed for application in methanol-to-olefins (MTO) reaction. *Microporous and Mesoporous Materials,* Volume 203, pp. 41–53

Zhang, L., Song, Y., Li, G., Zhang, Q., Zhang, S., Xu, J., 2012. F-assisted synthesis of hierarchical zsm-5 zeolite for methanol to propylene reaction: b-oriented thinner dimensional morphology, *RSC Advances*, Volume 5(75), pp.61354–61363