ISSN 1070-4272, Russian Journal of Applied Chemistry, 2019, Vol. 92, No. 8, pp. 1094−1101. © Pleiades Publishing, Ltd., 2019.

CATALYSIS

Ethylene to Propylene Conversion over Ni-W/ZSM-5 Catalyst

Ehsan Kianfar[a,b,*]

[a] Department of Chemical Engineering, Arak Branch, Islamic Azad University, Arak, Iran
[b] Young Researchers and Elite Club, Gachsaran Branch, Islamic Azad University, Gachsaran, Iran
*e-mail: e-kianfar94@iau-arak.ac.ir

Received February 1, 2019; revised June 25, 2019; accepted July 3, 2019

Abstract—A ZSM-5 base is used to produce light olefins in the process of converting ethylene to propylene, as well as Ni-W/ZSM-5 to improve the catalyst. After loading the Ni-W/ZSM-5 0.5,1,2 wt % by inoculation, the modified catalyst was investigated for accurate determination of the specification by SEM, BET, FTIR analyzes. The activity of this catalyst was evaluated in the process of ethylene to propylene conversion in a constant reactor under operational conditions (temperature 400°C, pressure 1 atm, and feed flow rate of 0.5 cm^3/min of pure ethylene), which also shows the results of tests of catalyst activity evaluation. The selectivity of ethylene and propylene over the modified catalyst will increase as the temperature rises and the maximum selectivity will be achieved at 400°C. The catalyst with 0.5 wt % Ni/ZSM-5 has the highest conversion rate and better selectivity than that with other percentages, also the catalyst with 2 wt % Ni-W/ZSM-5 has the highest conversion rate and better selectivity than other percentages.

Keywords: ethylene, propylene, fixed-bed reactor, catalyst ZSM-5, modified catalyst, Ni-W/ZSM-5

DOI: 10.1134/S1070427219080068

INTRODUCTION

Light olefins (ethylene and propylene), are considered among the most crucial elements in petrochemical industries, which are used for producing polymers and diverse chemicals. As the main feed of petrochemical processes, propylene is widely used. Olefins can be produced through diverse processes and different raw materials. The common point of all these processes is production in a wide range of products and peripherals. In addition to mentioned industrial processes, there exist additional non-industrial technologies in diverse development steps including oxidative coupling of methane (OCM), propane dehydrogenation (PDH) for production of propylene, low-value heavy olefins cracking exemplary C4/C5, metathesis of ethylene and butylene to propylene, and conversion of methanol to light olefins (MTP, MTO). Concerning access to hydrocarbon resources in different countries, diverse strategies are selected for production of olefins so that upon discovery of such strategies, propylene to ethylene ratio has been considerably decreased in steam cracking units and this has resulted in complicated propylene market. Although thermal cracking of naphtha is the main process of light olefins production such as propylene, such technologies as fluid catalytic cracking (FCC) and thermal cracking of ethane are classified as the methods with low efficiency. The effects of acidity, pore size, pore structure, and crystal size of the zeolite, as well as effect of operation reaction conditions upon product selectivity, has been investigated. These investigations was explained in [1]. World reserves of natural gas are approved to be over 5 000 trillion cubic feet which are being grown with a speed higher than that of approved reserved of crude oil. Current gas reserves are about 83% equivalent to the energy of approved oil reserves while 75% of these reserves are occupied to crude oil with lower suitability [2, 3]. About 3 000 trillion cubic feet of gas reserves are recognized as stranded reserves due to the economically unsustainable transition to consumer markets [3, 4]. Catalytic conversion of methanol to hydrocarbons is promising and indirect process to convert natural gas reservoirs to such valuable products as gasoline and olefins [5–10]. The changes made to the demand for petroleum products and petrochemicals with better properties have had a significant impact on the role of refinery and petrochemical processes in the former industry and it is even expected that this will be even more significant in the future. Therewith, in order to satisfy the required changes, some researchers plan to use

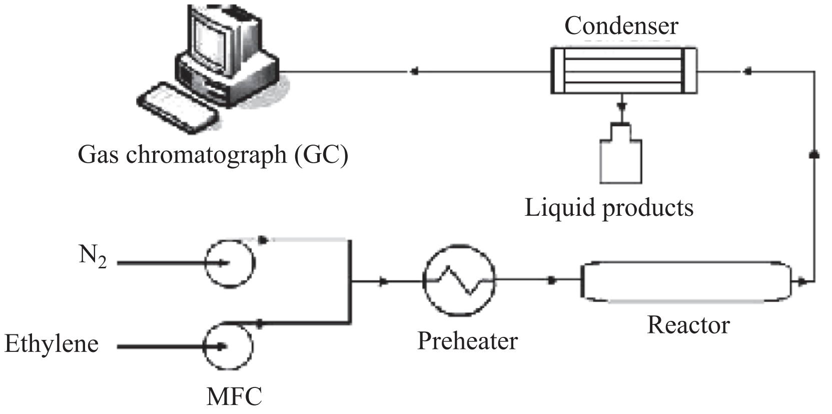

Fig. 1. Schematic diagram of experimental setup.

new and more important technologies with new catalysts. One of the most efficient methods is catalytic cracking in the vicinity of zeolites. During the recent decade, the advances in FCC area were considered in the sections of alumina technology and stability of zeolite as well as of acceptable limits of catalyst poisoning. The recent advances in the catalyst technology meet environmental regulations for illegal materials emissions such as SO_x, CO, and NO_x. In addition, controlling the selectivity of light olefins has been enhanced due to recent advances in stabilization and combination of ZSM-5 basic additives [5–15]. Since catalytic cracking has been recognized as an alternative way to produce light olefins, although this process is still in the development step, the results show that catalytic cracking provides more advantages compared to thermal cracking. The most important features of catalytic cracking include the higher capacity to produce ethylene and propylene, lower emissions of greenhouse gases, considerable energy saving as well as the capability to reduce invaluable heavy products [16]. In this section, the cracking process will be discussed initially and then catalytic cracking of olefins preparation will be pointed out [17–20, 34–36]. Overview of catalytic results for the ethylene to propylene reaction using selectivity zeolite catalysts is in Table 1. Zeolites as catalysts have many unique properties such as acidity, shape-selectivity, high surface area and structural stability. The destination of this article is using the ZSM-5 catalytic process for producing light olefins. The purpose of this work is to synthesize and determine the characteristics of Ni/SM-5 and W/ZSM-5 catalysts and evaluate their role in the conversion of ethylene to propylene. Therewith, the direct conversion of ethylene to propylene can be an effective way to respond to global demand. In the study ethylene was used as a feed. In addition, insemination of the modified zeolite with nickel and tungsten leads to the production of propylene with a higher conversion rate and selectivity.

EXPERIMENTAL

Materials. Sodium aluminate (technical grade) was purchased from Riedel-deHaen. Silicic acid (96.6%), tetrapropylammonium bromide (98%), sodium hydroxide (97.5%), methanol (99.9%), ethanol (96%), ammonium nitrate (99.95%), ethylene (99.9%), nickel(II) nitrate (99%), sodium tungstate (99%) were supplied by Merck. All materials used were of experimental purity grade and suitable purity.

ZSM-5 catalyst synthesis. Initially the desired amount of sodium aluminate was added to hydroxide sodium solution and stirred for 60 min (solution A). In another beaker, required amount of *tetra*-propyl-ammonium bromide was added to sodium hydroxide solution and stirred for 30 min. Silicic acid and deionized water were slowly added and stirred for another 30 min (solution B). Subsequently, solution A was mixed with solution B and stirred for 60 min. Final gel was transferred to a Teflon-lined stainless steel autoclave and heated at 180°C for 12 h. Finally, contents of reactor were filtered, washed, and dried at 110°C for 12 h. The solid product was calcined at 500°C for 5 h. Ion exchanging of ZSM-5 zeolite was performed using ammonium nitrate solution (1 M). Zeolite was mixed with solution and heated at 110°C for 6 h. In the following step, silica foam was added to the solution while mixing. After 24 h of mixing, the derived gel was poured into an autoclave reactor and heated at

Table 1. Role of reaction parameters during ETP reaction with zeolite catalysts

Zeolite	Si/Al	T, °C	C_1–C_4, wt %	$C_{3=}$, wt %	$C_{4=}$, wt %	C_{5+}, wt %	BTX, wt %	References
Ni/MCM-41	–	400	–	48.0	43.0	<5	–	[23]
Ni/MCM-41	60	450	–	44.0	54.0	–	–	[24]
Ni/MCM-48	–	350	–	56.0	35.0	8	–	[25]
NiRe/γ-Al_2O_3	–	50	–	49.0	50.0	–	–	[26]
Ni/silica-alumina 12-MR	223	375	–	32.0	56.0	–	–	[27]
Beta	25	450	28.1	47.5	14.4	10.0	0	[28]
Beta	27	550	69.1	14.1	5.1	3.8	7.9	[29]
Beta	11.4	450	25.7	43.4	20.8	10.1	-	[30]
Mordenite	11.2	400	25.8	38.5	21.2	14.5	-	[30]
MCM-22	20	450	15.9	43.8	40.3	0	0	[31]
UZM-35[a]	8.9	400	19.3	31.5	25.8	16.2	7.2	[29]
EU-1	33	550	13.2	45.4	21.1	14.7	5.6	[30]
EU-1	10.3	400	26.5	32.3	22.3	18.9	-	[30]
ZSM-11	35	550	38.2	19.1	8.7	4.9	29.1	[29]
ZSM-22	35	550	6.3	41.8	28.3	20.5	3.1	[29]
ZSM-23	34	550	8.9	43.4	24.4	18.4	4.9	[31]
SAPO-44[b]	0.1	450	10.8	75.4	10.0	3.8	0	[31]
SAPO-34[b]	0.1	450	7.8	84.7	7.5	0	0	[31]
SAPO-34[b]	0.1	400	22.4	68.3	7.7	1.6	–	[31]
SAPO-34[b]	0.08	400	12.0	63.0	16.0	9.0	–	[30]
SAPO-34[b]	0.1	450	6.6	79.5	12.1	1.8	–	[30]
SAPO-18[b]	0.1	450	9.1	78.7	12.2	0	0	[32]
SAPO-18[b]	0.3	500	14.0	40.0	24.0	20.0	2.0	[33]

[a] K/Al = 0.09.

[b] Si/(Si + Al + P).

150°C for 6 days. Catalyst was dried at 110°C for 12 h and calcined at 500°C for 5 h [21, 22].

Preparation of catalyst Ni/ZSM-5. An appropriate amount of 0.07 g nickel nitrate salt was used to make third catalysts with 0.5, 1, and 2 wt % of Ni on ZSM-5 zeolite. For each sample, 5 g salt was mixed with 2 cm^3 water in a beaker. ZSM-5 (0.05 g) was then added to the solution and pH was adjusted to 5 using the ammonia solution (1 M). When the pH became stable, the mixture was placed in an ultrasonic bath for 180 min. The resultant product was filtered, washed, and dried at 110°C for 24 h and calcined at 650°C for 3 h.

Preparation of catalyst Ni-W/ZSM-5. An appropriate amount (0.155 g) of nickel nitrate and tungsten nitrate salt

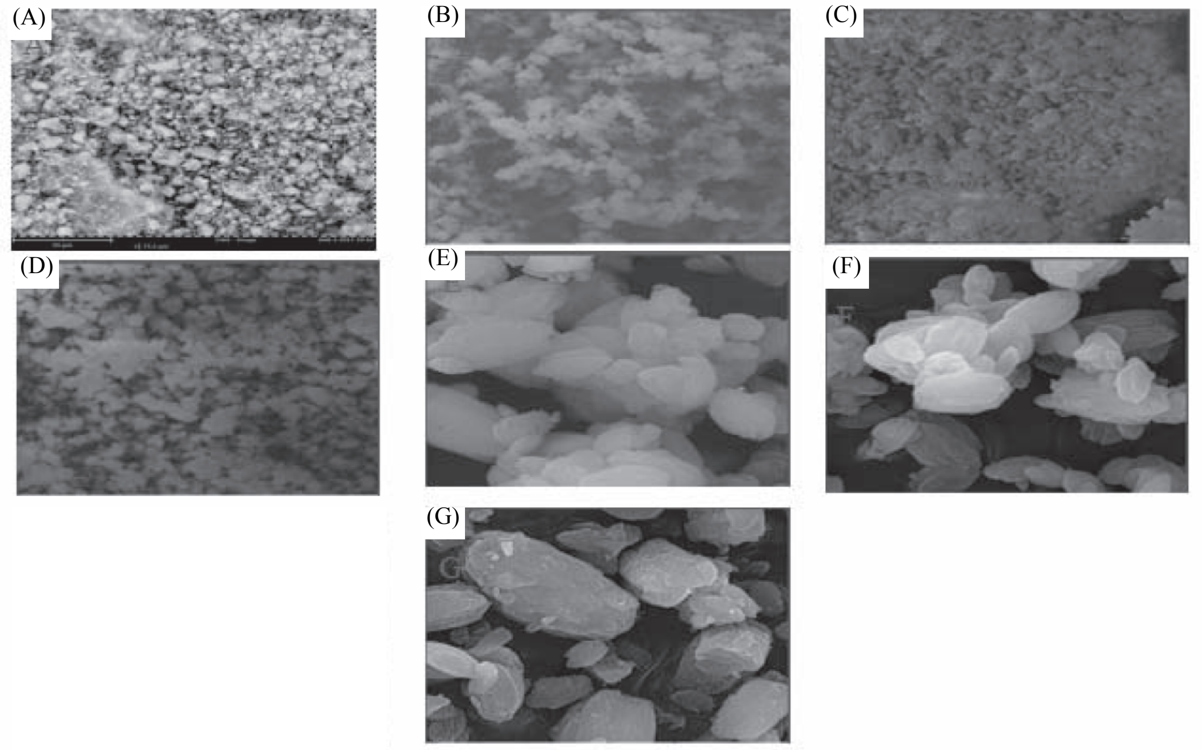

Fig. 2. SEM analysis: (A) ZSM-5, (B) 0.5 wt % Ni/ZSM-5, (C) 1 wt % Ni/ZSM-5, (D) 2 wt % Ni/ZSM-5, (E) 0.5 wt % Ni-W/ZSM-5, (F) 1 wt % Ni-W/ZSM-5, (G) 2 wt % Ni-W/ZSM-5.

was used to make third catalysts with 0.5, 1, and 2 wt % of Ni-W on ZSM-5 zeolite. For each sample, 5 g salt was mixed with 2 cm^3 water in a beaker. ZSM-5 (0.10 g) was then added to the solution and pH was adjusted to 5 using the ammonia solution (1 M). When the pH became stable, the mixture was placed in an ultrasonic bath for 180 min. The resultant product was filtered, washed, and dried at 110°C for 24 h and calcined at 650°C for 3 h.

Catalytic tests. Figure 1 shows ETP of the experimental rig. Conversion of ethylene to propylene was carried out in a fixed-bed reactor. For each experiment, 1.2 g of catalyst sample was placed in a stainless steel tube (L: 500mm, ID: 7mm), and held in its place with glass wool. Subsequently, a reactor was placed inside of a tabular furnace, which was controlled by a PID temperature controller. All experiments were carried out at the temperature of 400°C and pressure of 1 bar. Nitrogen was used as carrier gas for ethylene as well as providing better distribution of reactant. Products are passed through a condenser, which is held in cool water to reduce the temperature of the effluent gas. Subsequently, gas and liquid products are separated in a small cylinder. Liquid products were analyzed using an online GC equipped with an FID indicator and Petrocol® DH capillary column (L.: 100 m, Dia.: 0.25 mm, film thickness: 0.5 μm) and helium as a carrier gas.

RESULTS AND DISCUSSION

SEM analysis results. Figure 2 shows SEM analysis results for the calcined catalyst, which were photographed with a zooming of 20 μm. The SEM analysis was used to evaluate the morphology of modified catalysts. As it can be seen in Fig. 2, the catalysts of 0.5, 1, 2% Ni/ZSM-5, 0.5, 1, and 2% Ni-W/ZSM-5 with a Si/Al ratio of 15 have a fully porous and spongy structure.

Results of FT-IR analysis. Figure 3 depicts the results of FTIR on the catalysts 0.5, 1, 2% Ni/ZSM-5, 0.5, 1, 2% Ni-W/ZSM-5 with a Si/Al ratio of 15 in the area of 400 to 2000 cm^{-1}. The peak in the area 450 cm^{-1} is associated with Si–O–Si and Al–O–Al bonds and the peaks 790 and 1100 cm^{-1} are, respectively, associated with symmetric and asymmetric T–O–T bonds in the structure of zeolite while T can be either Al or Si in the structure of the zeolite. The peaks 790 and 1100 cm^{-1} are seen at almost all zeolites or crystalline materials

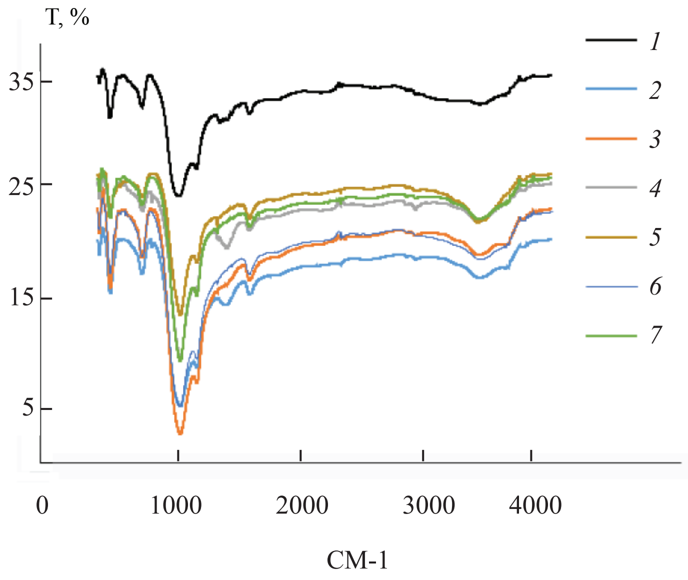

Fig. 3. (Color online) FTIR analysis pattern results for prepared catalyst. (*1*) ZSM-5, (*2*) 0.5 wt % Ni/ZSM-5, (*3*) 1 wt % Ni/ZSM-5, (*4*) 2 wt % Ni/ZSM-5, (*5*) 0.5 wt % Ni-W/ZSM-5, (*6*) 1 wt % Ni-W/ZSM-5, (*7*) 2 wt % Ni-W/ZSM-5.

Table 2. BET results for different synthesized catalysts

Catalysts	BET surface area, m^2 g^{-1}	Pore volume, cm^3 g^{-1}
ZSM-5	300	0.39
Ni / ZSM-5 (0.5%)	286.97	0.33
Ni / ZSM-5 (1%)	270.02	0.31
Ni/ ZSM-5 (2%)	272.15	0.30
Ni-W/ ZSM-5 (0.5%)	257.38	0.35
Ni-W/ ZSM-5 (1%)	271.97	0.33
Ni-W/ ZSM-5 (2%)	275.85	0.31

containing silicon. The peaks available in 545 and 620 cm^{-1} indicate MFI structure and are visible only in the zeolites with MFI structure. The peaks appeared in the areas 1633 and 3451 cm^{-1} are, respectively, associated with stretching vibration frequency of Al–O bond and that of hydroxyl group for the bond between Si and Al atoms. The acidity of OH group in the area 3000 cm^{-1} means a high absorptive frequency which has been appeared. Accordingly, a sharp peak of OH group was removed

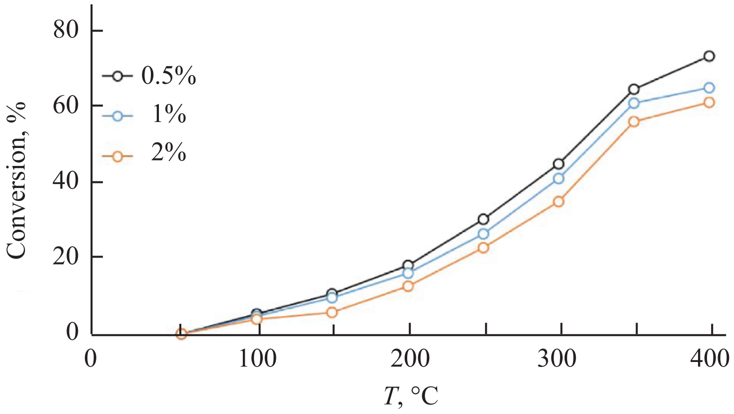

Fig. 4. (Color online) Effect of temperature on the rate of ethylene conversion by Ni/ZSM-5 catalyst.

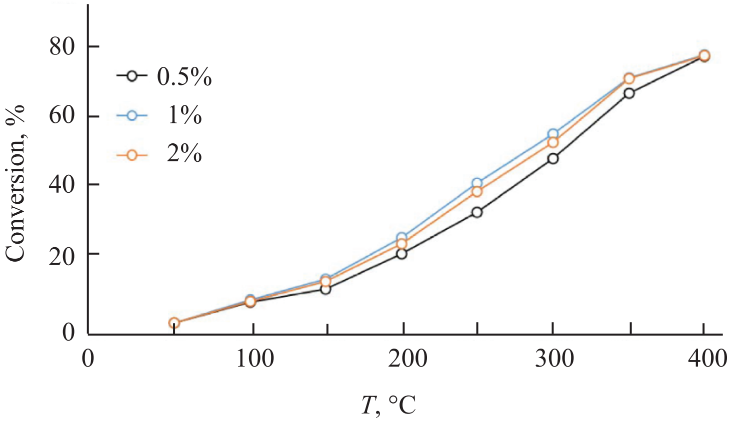

Fig. 5. (Color online) Effect of temperature on the rate of ethylene conversion by Ni-W/ZSM-5 catalyst.

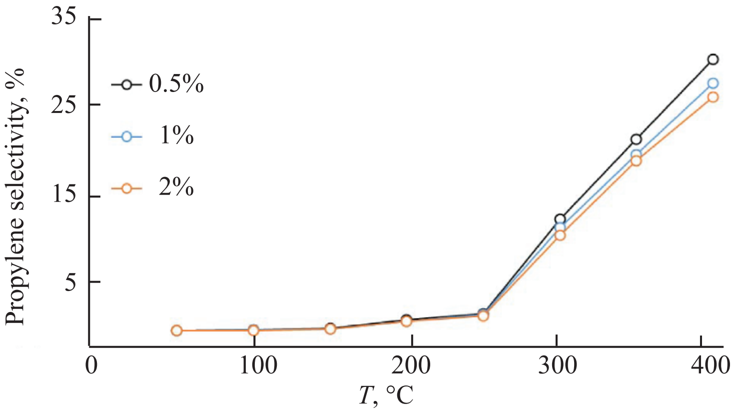

Fig. 6. (Color online) Effect of temperature on the selectivity of propylene with Ni/ZSM-5.

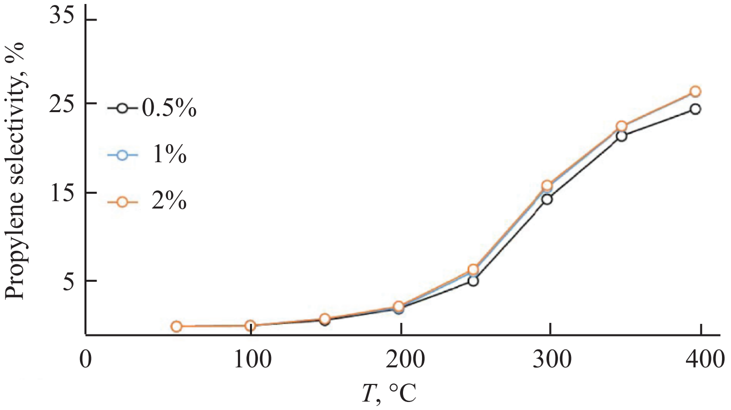

Fig. 7. (Color online) Effect of temperature on the selectivity of propylene with Ni-W/ZSM-5 catalyst.

in the area 3600 cm^{-1}, which is associated with Al–OH group, indicating removal of OH group and formation of Ni–O. If a peak has appeared for Ni–O and W–Ni–O compounds, then it should have appeared in the area 400–450 cm^{-1} which can be overlapped with the peaks Si–O–Si and Si–O–Al.

Results of BET analysis. Table 2 presents physical and chemical properties of the catalyst of ZSM-5 and Ni/ZSM-5 and Ni-W/ZSM-5 using BET analysis. Also, BET analysis was conducted to be informed of specific surface, size, and volume of pores. The specific surface of the catalyst of Ni/ZSM-5 decreased from 286.97 to 272.15 m^2 g^{-1} through increased amount of Ni from 0.5 to 2%. Also, total pores volume decreased from 0.33 to 0.30 cm^3 per gram through increased amount of Ni from 0.5 to 2%, as well. The specific surface of the catalyst of Ni-W/ZSM-5 increased from 257.35 to 275.85 m^2 g^{-1} through increased amount of Ni-W from 0.5 to 2%. Total pores volume decreased from 0.35 to 0.31 cm^3 g^{-1} through increased Ni-W from 0.5 to 2%, as well.

The effect of temperature on rate of ethylene conversion by Ni/ZSM-5 catalyst. Figure 4 shows conversion rate of ethylene according to temperature using Ni/ZSM-5 catalysts with 0.5, 1, and 2 wt %. The percent conversion of ethylene to propylene at various temperatures with Ni modified ZSM-5 catalysts is shown in Fig. 4. With increasing temperature, the percentage of ethylene conversion increases and the ascending trend is observed. The maximum conversion rate can be seen at 400°C and the lowest conversion rate, at 50°C. The catalyst with 0.5% Ni has the highest conversion rate than those of other percentages.

The effect of temperature on rate of ethylene conversion by Ni-W/ZSM-5 catalyst. Figure 5 shows conversion rate of ethylene vs. temperature using Ni-W/ZSM-5 catalysts with 0.5, 1 and 2 wt %. The percent conversion of ethylene to propylene at various temperatures with Ni-W modified ZSM-5 catalysts is shown in Fig. 5. With increasing the temperature, the percentage of ethylene conversion increases and the ascending trend is observed. The maximum conversion rate can be seen at 400°C and the lowest conversion rate at 50°C. The catalyst with 2 wt % Ni-W has the highest conversion rate than those of other percentages.

The effect of temperature on selectivity of propylene by Ni/ZSM-5 catalyst. Figure 6 presents an effect of temperature on the selectivity of propylene on the ZSM-5 catalysts modified by Ni. Figure 6 shows diagram of selectivity in terms of temperature using Ni/ZSM-5 catalysts with 0.5, 1 and 2 wt %. In this regard, with increasing temperature from 250°C, selectivity rate is enhanced with an increasing trend. The highest and lowest selectivity can be seen at 400°C and 50–150°C range. The catalyst with 0.5 wt % Ni has the highest selectivity than those of other percentages.

The effect of temperature on selectivity of propylene by Ni-W/ZSM-5catalyst. Figure 7 presents an impact of temperature on the selectivity of propylene on the ZSM-5 catalysts modified with W. Figure 7 shows diagram of selectivity in terms of temperature using Ni-W/ZSM-5 catalysts with 0.5, 1, and 2 wt %. In this regard with increased temperature from 250°C, selectivity rate is enhanced with an increasing trend. The highest and lowest selectivity can be seen at 400 and 50–100°C range. As seen in the catalyst with 2 wt % Ni-W has the highest selectivity than those of another percentages.

CONCLUSIONS

Zeolite ZSM-5 was used as a catalytic base for production of light olefins. Also, the metals nickel and tungsten were employed to improve catalyst performance. The results of catalytic cracking using the mentioned catalyst showed increased selectivity of light olefins compared to thermal cracking in diverse temperatures. The analyses XRD, BET, FTIR, and SEM were conducted on some of the modified samples which indicated that the catalyst structure was not disrupted. The test design was hired to evaluate the performance of the catalyst in ethylene to propylene conversion and impact of loading parameters of nickel-tungsten. The results indicated that selectivity of ethylene and propylene on a catalyst by nickel and tungsten will be accompanied by increasing trend of temperature such that the highest selectivity is derived in a temperature of 400°C.

FUNDING

Funding there is no funding to report for this submission.

CONFLICT OF INTEREST

Conflict of interest the authors declare that they have no conflict of interest

REFERENCES

1. Aishah, N. and Amin, S., *J. Natural Gas Chem.*, 2003, vol. 12, p. 123.
2. Alvarado Perea, L., Wolff, T., Veit, P., Hilfert, L., Edelmann, F.T., Hamel, C., and Seidel, M.A., *J. Catal.*, 2013, vol. 305, p. 154.
3. Dai, W., Sun, X., Tang, B., Wu, G., Li, L., Guan, N., and Hunger, M., *J. Catal.,* 2014, vol. 314, p. 10.
4. Epelde, E., Ibañez, M., Aguayo, A.T., Gayubo, A.G., Bilbao, J., and Castaño, P., *Microp. Mesop. Mater.*, 2014, vol. 195, p. 284.
5. Frey, A.S. and Hinrichsen, O., *Microp. Mesop. Mater.*, 2012, vol. 164, p. 164.
6. Follmann, S. and Ernst., S., *New J. Chem.,* 2016, vol. 40, p. 4414.
7. Galvis., H.M.T., Bitter, J.H., Davidian, T., Ruitenbeek, M., and Dugulan, A.I., *J. Am. Chem. Soc.*, 2012, vol. 134 , p. 16207.
8. Han, S.Y., Lee, C.W., Kim, J.R., Han, N.S., Choi, W.C., Shin, C.H., and Park, Y.K., *Fuel*, 2014, vol. 153, p. 157.
9. Henrique Zandonai, C., Hissae Yassue-Cordeiro, P., Berenice Castellã-Pergher, S., Heloisa Neves Olsen Scaliante, M., and Regina Camargo Fernandes-Machado, N., *Fuel*, 2016, vol. 172, p. 228.
10. Ibanez, M., Gamero, M., Ruiz-Martinez, J., Weckhuysen, B.M., Aguayo, A.T., Bilbao, J., and Castano, P., *Catal. Sci. Technol.*, 2016, vol. 6, p. 296.
11. Iwamoto, M., *Catal. Surv. Asia*, 2008, vol. 12, p. 28.
12. Jang, H., Min, H., Hong, S., and Seo, G., *J. Catal.*, 2013, vol. 299, p. 240.
13. Jang, H., Ha, K., Kim, J., Sugi, Y., and Seo, G., *Appl. Catalysis A: General,* 2014, vol. 476, p. 175.
14. Kianfar, E., *Indian J. Sci. & Techn.,* 2015, vol. 8, p. 455.
15. Kianfar, E., Baghernejad, M., and Rahimdashti, Y., *J. Biolog. Forum,* 2015, vol. 7, p. 1671.
16. Kianfar, E., Salimi, M., Pirouzfar, V., and Koohestani, B., *Int. J. Appl. Ceram. Technol.,* 2018, vol. 15, p. 734.
17. Kianfar, E., Salimi, M., Pirouzfar, V., and Koohestani, B., *Int. J. Chem. Reactor Eng.,* 2018, vol. 16(7), p. 1.
18. Lee, J., Hong, U., Hwang, S., Youn, M., and Song, I., *Fuel ProNissing Technology*, 2013, vol. 109, p. 189.
19. Li, L., Palcheva, R.D., and Jens, K., *Top. Catal.*, 2013, vol. 56, p. 783.

20. Lin, B., Zhang, Q., and Wang, Y., *Ind. Eng. Chem. Res.*, 2009, vol. 48, p. 10788.
21. Lee, K., Cha, S.H., and Hong, S.B., *ACS Catal.*, 2016, vol. 6, p. 3870.
22. Maia, A.J., Oliveira, B.G., Esteves, P.M., Louis, B., Lam, Y.L., and Pereira, M.M., *Appl. Catal. A: General,* 2011, vol. 403, p. 58.
23. Majhi, S. and Pant, K.K., *J. Ind. & Eng. Chem.,* 2014, vol. 20, p. 2364.
24. Oikawa, H., Shibata, Y., Inazu, K., Iwase, Y., Murai, K., Hyodo, S., Kobayashi, G., and Baba, T., *Appl. Catal., A*,.2006, vol. 312, p. 181.
25. Ofei, D., Mante, F.A., and Agblevor, R., *Fuel*, 2013, vol. 108, p. 451.
26. Stoyanova, M., Schneider, M., and Pohl, M., Rodemerck, U., *Catal. Commun.*, 2017, vol. 92, p. 65.
27. Themba, E., Tshabalala, E.M., and Scurrell, S., *Catal. Commun.,* 2015, vol. 72, p. 49.
28. Wei, Y.X., Zhang, D.Z., He, Y.L., Xu, Y., Yang, L., Su, B.L., and Liu, Z.M., *Catal. Lett.,* 2007, vol. 114, p. 30.
29. Xu, R., Liu, J., Liang, C., and Wen, H., *J. Fuel Chemistry & Technology*, 2011, vol. 39, p. 449.
30. Xue, T., Zhang, Q., and Song, H., *J. Catal.,* 2012, vol. 295, p. 232.
31. Xue, N., Nie, L., Fang, D., Guo, X., Shen, J., and Ding, W., *Appl. Catal. A: General*, 2012, vol. 352, p. 87.
32. Yaripour, F., Shariatinia, Z., and Sahebdelfar, S., *J. Nat. Gas Sci. Eng.*, 2015, vol. 22, p. 260.
33. Zheng, A., Zhao, Z., Chang, S., and Huang., Z., *J. Molecular Catalysis A: Chemical,* 2014, vol. 383, p. 23.
34. Kianfar, E., *Russ. J. Appl. Chem*., 2018, vol. 91(10) , pp. 1711–1720.
35. Kianfar, E., Salimi, M., Hajimirzaee, S., and Koohestani, B., *Int. J. Chem. React. Eng*., 2018, https://doi.org/10.1515/ijcre-2018-0127.
36. Kianfar, E., *Microchem. J.,* 2019, 145, pp. 966–978.