IRANIAN JOURNAL OF CATALYSIS

Non-oxidative conversion of methane to aromatics over modified zeolite catalysts by transitional metals

Elmira Yaghinirad[a], Hassan Aghdasinia[a,*], Ali Naghizadeh[a], Aligholi Niaei[a]

Faculty of Chemical and Petroleum Engineering, University of Tabriz, 51666-16471 Tabriz, Iran.

ABSTRACT

In this study, the activity of different transitional metals over modified H-ZSM-5 catalysts for methane conversion to aromatics was compared. The first group of catalysts was Mo-impregnated H-ZSM-5 zeolites with 1, 3 and 6 wt% of Mo. The second group was M (3 wt%)- impregnated H-ZSM-5 (M: Ag, Cd, Cr, Mo, Zn and Mn). The catalytic activity of the first group was investigated at temperature of 600, 700 and 800 °C and gas hourly space velocity (GHSV) of 1500, 2250, 3600 [ml.g^{-1}.h^{-1}]. Likewise, the second group of catalysts was examined at 700 °C and GHSV of 2250 [ml.g^{-1}.h^{-1}]. The catalyst samples were appropriately characterized by XRD, BET and SEM techniques. The effect of loaded transitional metals on the methane conversion was sorted on the basis of the benzene yield as follows: 3 %wt Mo> 3 %wt Zn> 3 %wt Mn> 3%wt Ag> 3%wt Cd > 3%wt Cr. The highest methane conversion was 11.13% obtained over the Mo (3 wt%)-impregnated HZSM-5 catalyst.

Keywords: Natural gas, Dehydro-aromatization, HZSM-5 metal-modified catalyst, Nonoxidative-conversion.

1. Introduction

The resources of oil are restricted; therefore, its producing and transferring expenses are increasing perpetually. If oil production and consumption rates grow with the current rates, the explored oil reservoirs fulfill just for ensuing 40-50 year [1]. Because of the limited reserves of oil, the energy resource is changing from oil based to gas based [2].

The global dependence on crude oil is reduced by using GTL (Gas to Liquid) technologies. They also offer significant opportunities for gas industries to supply the liquid-gas products. In the next 100-150 years, the world natural gas reserves might become the main resources for production of organic compounds that are generated currently from oil. The development of chemical processes in natural gas conversion solves the problem of raw materials for the petrochemical industry [1].

Within the 21st century, natural gas will be the foremost necessary supply of energy, moveable liquid fuels and petrochemicals [3,4]. Natural gas is indirectly and directly converted into precious chemicals (Fig. 1).

Natural gas is transformed via a derivative of methane such as synthesis gas (a compound of H_2 and CO) or methanol, to the final products in the indirect method.

The direct utilization of CH_4, the main component of natural gas (NG), as an alternate chemical feedstock to petroleum, is highly desirable but difficult in industrial catalysis. Many direct and indirect ways have been discussed for CH_4 conversion into more beneficial products, including ethylene hydrocarbons, higher molecular weight hydrocarbons and liquids (e.g. gasoline) [5].

For indirect petrochemical industry, natural gas is connected primarily to the production of syngas. Recently, scientists focused on the oxidation of CH_4 to ethylene (OCM) [4].

Some of the researchers endeavored to find a way to convert methane to higher hydrocarbons by oxygen-free processes. It was reported that methane could be converted to benzene with using a transitional metal-loaded catalyst and passing CH_4 over that at 977K for 30 min [6].

Zeolites are aluminosilicate solids which are microporous and crystalline. Zeolites structures are well-defined. Generally, silicon, aluminum and oxygen are the main elements in their framework and within

*Corresponding author.

E-mail addresses: aghdasinia@tabrizu.ac.ir; hassan.aghdasinia@gmail.com (H. Aghdasinia)
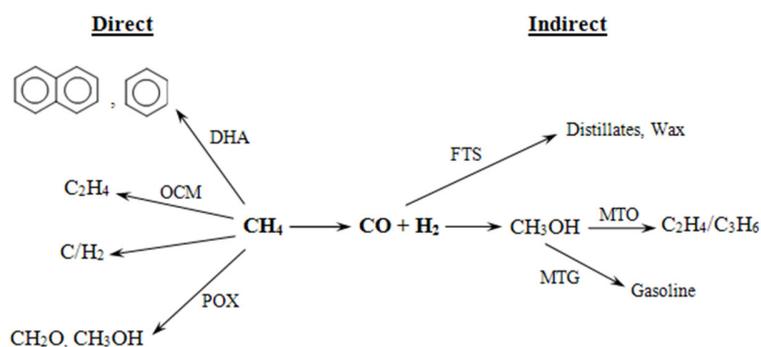
Fig. 1. Main paths from natural gas to value-added products: MDA (methane dehydroaromatization), POX (partial oxidation), OCM (oxidative coupling of methane), MTG (methanol-to-gasoline), MTO (methanol to olefins), and FTS (Fischer-Tropsch synthesis).

their pores cations, are formed by water and/or other molecules. They are widely used in methane conversion because of their high crystallinity, low and high availability of acid sites, temperature stability and a large surface to ensure selective reactions in catalyst science. Structurally, zeolites with pore diameters of 5-6 Å are appropriate for the methane conversion [7].

Methane conversion in the lack of oxygen was studied for the first time in 1993 by Wang [8]. He prepared Mo loaded HZSM-5, and studied the methane catalytic reaction to aromatics at 973 K in the lack of oxygen. A fixed bed reactor was used for this process. The conversion was low, but too high in selecting benzene. Because of the excessive significance of zeolite supported catalysts in this reaction, the study of the catalyst modification, active site and/or phase, the interaction between the metal part and the zeolite support, the procedure of the reaction and carbonaceous formation residue and their function in the methane dehydro-aromatization (MDA) became serious subjects.

The primary goal of researchers in this area has been to expand effective, efficient and environmentally benign processes to utilize the natural gas. Controlling the methane C−H bond activation and the selective formation of C−C bonds have been common and extremely important topics in both homogeneous and heterogeneous catalysis. Due to its kinetic inertness, methane activation is considered a too challenging problem. Generally, transition metal plays a pivotal role in this reaction and the substantial mechanistic discernment has been obtained from the studies including homogeneous catalysts. Future approaches are likely to be built on our rapidly expanding molecular knowledge about the chemistry of transition metals, homogeneous catalysis and graphene growth to interpret the nature and mechanism of MDA reaction over Molybdenum-loaded catalysts.

So far, the best catalysts known for methane dehydro-aromatization are Molybdenum-containing zeolites [9].

This research aims to test the impact of loading different metals such as Ag, Cd, Cr, Mn and Zn on HZSM-5 and compare it with Mo on catalytic efficiency during methane non-oxidative conversion. The catalysts include 3% of each metal prepared by dry impregnation of the respective metal oxides on the HZSM-5. Also, the catalytic efficiency of different values of Mo-loaded on HZSM-5 was tested. Various temperatures and Gas Hourly Space Velocities (GHSV) were tested for 3 % wt Molybdenum-loaded on HZSM-5 catalyst.

2. Experimental

2.1. Catalyst preparation

The 3 wt% M/HZSM-5 (M is a precious metal such as Ag, Cd, Cr, Mo, Zn, Mn) and 1,3,6 wt% Mo/HZSM-5 catalysts were prepared by impregnation of HZSM-5 ($SiO_2/Al_2O_3 = 50$). Each metal oxide is dissolved in a small amount of nitric acid, and some ammonia is also used to dissolve molybdenum oxide. Then, 70 ml of distilled water was added to the solution, then a certain amount of zeolite was added to the solution in the form of HZSM-5 and stirred with a magnetic stirrer for 4 h, then followed by drying at 383 K over a night and calcination at 773 K for 5 h in air. All the metal oxides were provided from Merck. The catalyst was in the powder form.

2.2. Catalyst characterization

Powder XRD measurements were carried out using the D500 Ziemens diffractometer for phase identification and determination of the crystallinity. BET surface area analysis was used to compute the surface area, and t-plot analysis was used to measure the average pore volume. To detect the morphology of samples the SEM experiment was used. To avoid the charge influence of the samples, samples were covered with gold before the SEM analysis.

2.3. Catalytic test

0.5 g of catalyst was placed in the middle part of the continuous-flow fixed-bed quartz micro reactor of 1 cm ID, under atmospheric pressure of the catalytic test. The N$_2$ internal standard was entered into the reactor at 1500 [mLg^{-1}h^{-1}]. The temperature was raised to the desired temperature (600, 700, 800 °C) within 15 min concurrently, and was kept constant during the reaction. The feed gas was entered into the reactor at three different GHSV (1500, 2250, 3600 [mLg^{-1}h^{-1}]). A gas chromatograph (GC-17A) with a CBP5-M25-025 (Shimadzu) quartz capillary column was used to analyze the products, such as benzene, toluene, and naphthalene by the Flame-Ionization-Detector (FID). Then, the methane conversion, selectivity and yield of benzene could be calculated.

3. Results and Discussion

3.1. BET, XRD and SEM results

The other catalysts were all characterized by the fundamental analysis. Identification and determination of catalysts were done by XRD, crystallization increases when sharpness increases but the amorphous phase decreases.

The XRD pattern of HZSM-5 catalyst base with Si/Al=50 is given in Fig. 2 and matched those reported in typical zeolite structure reports [10]. As shown in Fig 2, the XRD pattern of HZSM-5 catalyst is compared with HZSM-5 catalyst modified with 3wt% Mn, Zn, Cr and Ag and showed that the location of the peaks does not change with the addition of metal to the zeolite structure and commonly overall crystallinity of zeolite does not considerably change as reported by Yang [10].

This study showed that the metal addition to the zeolite structure did not construct substantial changes in the overall zeolite crystallization and only incurred an insignificant decrease of peaks. There were no specific refraction peaks of metal oxide, this shows that the metal oxide spreads well on/in the HZSM-5 zeolite as reported by Yang [10]. As shown in Fig. 3, the X-ray diffractions of 1, 3 and 6% Mo/HZSM-5 catalyst were compared and the totality shape of the picks did not change as perceived by Tessonnier [11] and show that the Mo element either was on the outside surface of the zeolite crystals or diffused in inner part of its channels.
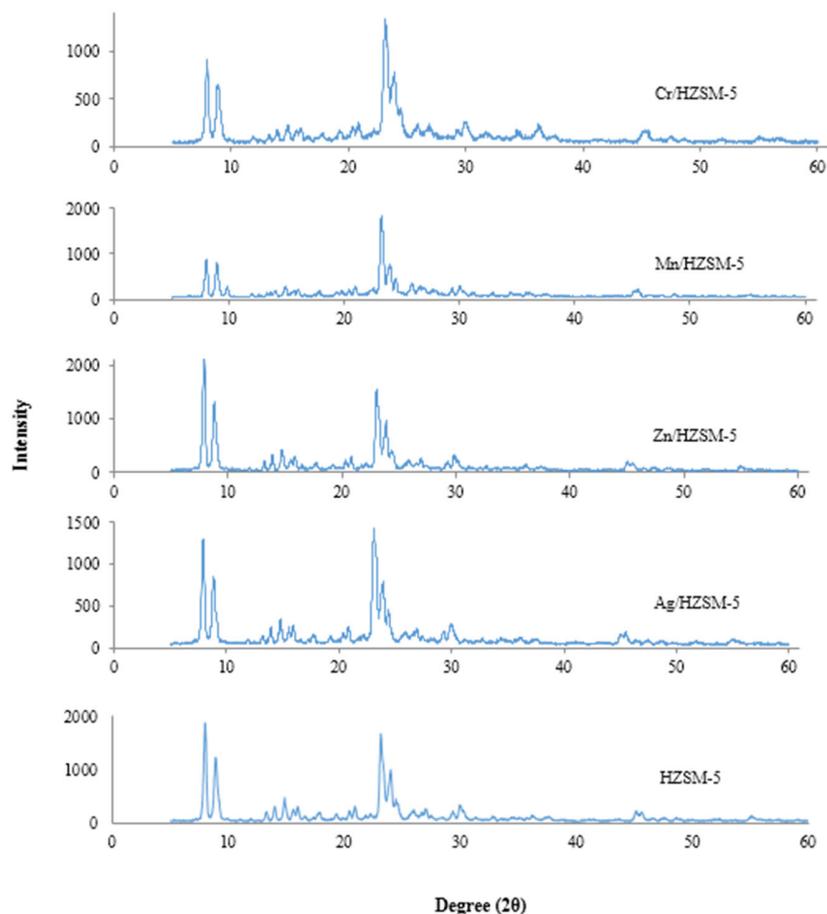
Fig. 2. XRD Patterns for the 3%Zn, 3%Mn, 3%Cr, 3%Ag /HZSM-5 and H-ZSM-5 catalysts.
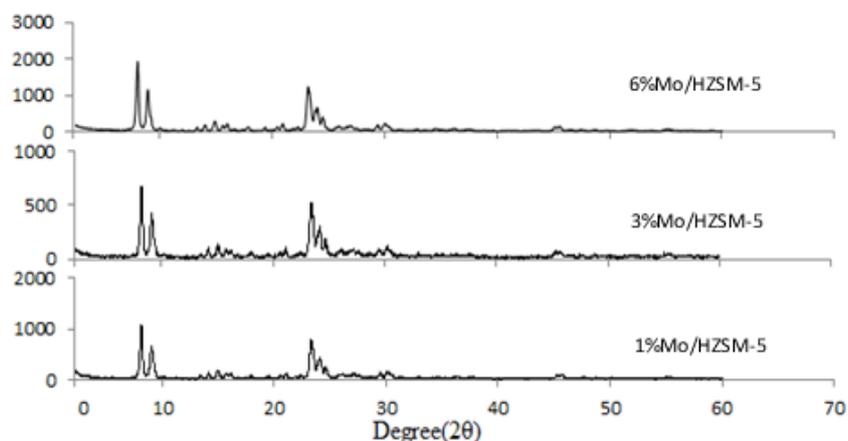
Fig. 3. XRD Patterns for the 1, 3, 6% Mo/HZSM-5 catalysts.

Results of BET analysis for HZSM-5 and Mo/HZSM-5 were demonstrated in Table 1. An insignificant decrease was detected in the BET surface area and micropore volume of MoO_3/HZSM-5. The decrease in specific surface area and micropore volume could be assigned to the Mo species statement within the channels of the HZSM-5 support.

As shown in Fig. 4, the SEM micrograph obviously confirms the cubical shape crystal of the ZSM-5 zeolite. Additionally, no amorphous material was detected in the zeolites, showing that the ZSM-5 zeolites had a high crystallinity as reported by Yang and Liu [10].

3.2. Methane conversion to aromatics

The changing methane to aromatics for different catalysts by increasing of time on stream (TOS) is shown in Fig. 5. In the initial period of the reaction, methane conversion increases with increasing TOS, and reaches a maximum at 45 min, when the maximum was obtained, the methane conversion decreased with TOS.

The yield of aromatics followed the same trend. The maximum conversion of methane extents to 11.13, 4.77, 5, 3.18, 2.82 and 2.16% by 3% Mo, 3% Zn, 3% Mn, 3% Ag, 3% Cd and 3% Cr/HZSM-5 catalysts, respectively.

Table 1. Results of BET analysis for HZSM-5.

Catalyst	HZSM-5	Mo/HZSM-5
BET Single point (m^2g^{-1})	300.77	288.23
BET Multi point (m^2g^{-1})	319.9	301.2
Micropore Volume (cm^3g^{-1})	0.178	0.170
Micropore surface area (m^2g^{-1})	432.7	422.2
Pore Volume (cm^3g^{-1})	0.133	0.112
Average pore width (nm)	5.27	5.49
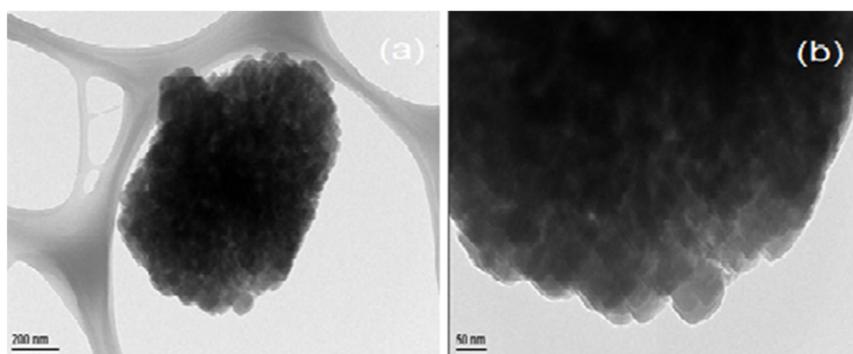
Fig. 4. SEM Patterns for HZSM-5 catalysts. (a) 200 nm, (b) 50 nm.
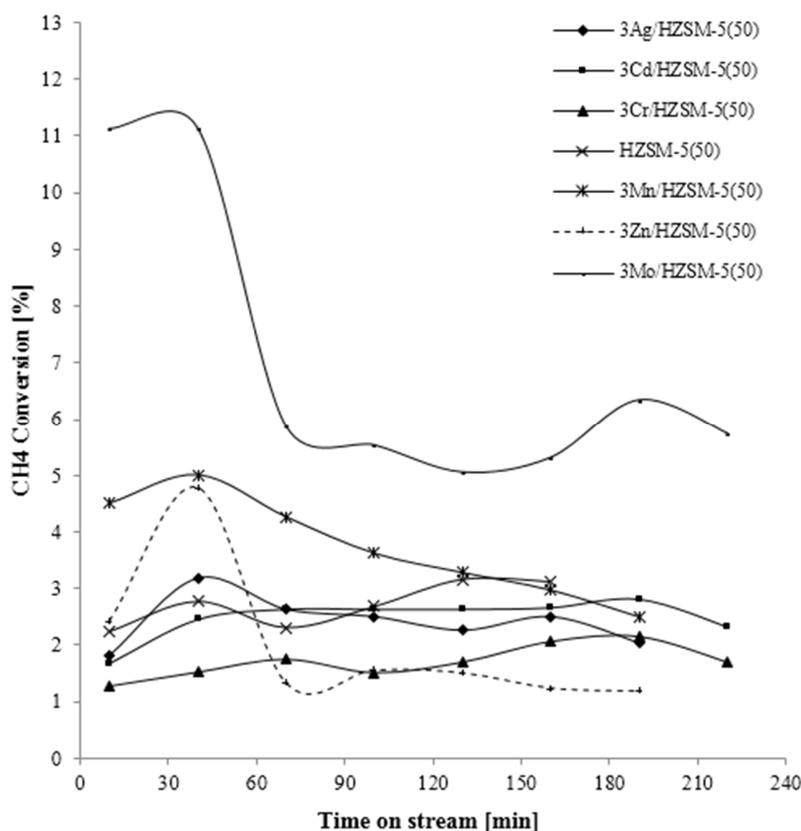
Fig. 5. Conversion of methane on different catalysts (T=700 °C, GHSV=2250 [mLg^{-1} h^{-1}], P=1 atm).

The methane conversion depends on the 10-ring 2D channel and Bronsted sites [8,12]. In addition, the supercages assistance the migration and transmission of loaded metals species into the channels associated with Bronsted acid sites and modifies stability and activity. Catalytic activities decrease by the time; heavy carbonaceous deposits on the catalyst formed during the methane direct aromatization were the main factors in decreasing the activities of the catalyst [9,13]. The yield of reaction decreased because of the reduction of strong acid sites.

Furthermore, the catalytic efficiency of this reaction is in the following order: 3%wt Mo > 3%wt Zn > 3%wt Mn > 3%wt Ag > 3%wt Cd > 3%wt Cr. Yield and selectivity of benzene after 45 min are shown in Fig. 6a and 6b, respectively. The benzene yields are 6.44, 3.99, 3.23, 2.36, 2.29 and 1.37% by 3% Mo, 3% Zn, 3% Mn, 3% Ag, 3% Cd and 3% Cr/HZSM-5 catalysts respectively. The catalytic performance of the 3%Mo/HZSM-5 for methane conversion to benzene clearly showed the maximum activity and selectivity compared to the other catalysts during the entire time on stream range, as reported by Skutil and Wang [4,8].

It is recognized that Mo is the best metal for this reaction, because CH$_4$ provides active sites to the formation of C$_2$H$_4$ from CH$_4$ by reducing the original Mo^{6+} ions to Mo$_2$C, and the acidic sites catalyze the last conversion to C$_6$H$_6$ [14-18]. The Mo$_2$C species are almost certainly spread on the external surface of the zeolite and a few of them are located in the channels of the zeolite. The Mo oxide species were extremely spread within the internal channels of the HZSM-5 [14,19].

The comparison of methane conversion over the different amounts of loaded Mo (1, 3, 6) %wt of Mo/HZSM-5 is shown in Fig. 7a and the comparison of reaction benzene yield was presented in Fig. 7b. As could be seen, when the content of loaded Mo was 1 wt%, methane conversion was low and yield of aromatics did not exceed 2% for all the time. If the amount of loaded Mo was up to 3wt%, the catalyst exhibited a desirable performance for methane aromatization, because as the loading of metal increases, the pores will be blocked and CH$_4$ cannot access the active sites [20].

The catalytic efficiency of catalysts to aromatic production is as follows: 3%wt Mo >6%wt Mo >1%wt Mo/HZSM. Methane conversion reached as high as 11.13%, and the maximal yield of aromatics was 6.44%. It is known that apart from the strong acid sites, species are also responsible for carbonaceous deposits creation [21].
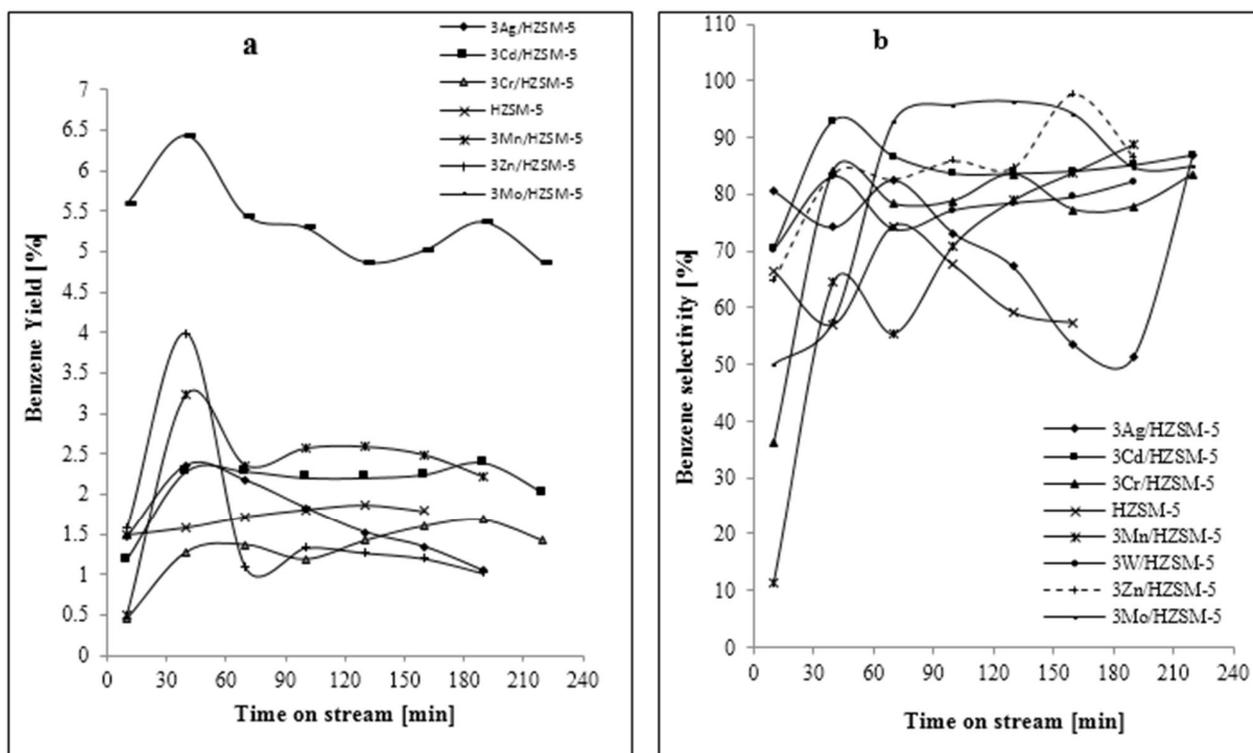
Fig. 6. a) Yield of benzene on different catalysts, b) Selectivity of benzene on different catalysts (T=700 °C, GHSV=2250 [mLg^{-1} h^{-1}], P=1 atm).

Increasing the Mo species loaded on HZSM-5, to 3wt% is positive for benzene formation and the maximal benzene yield was obtained. Consequently, the appropriate loaded of Mo in Mo/HZSM-5 catalyst for the MDA reaction is 3wt%.

The proportion of methane conversion at various temperatures (600, 700, 800 °C) on 3 %wt Mo/HZSM-5 catalysts is shown in Fig. 8a and the comparison of benzene yield of the reaction is shown in Fig. 8b. When the reaction temperature rose from 600 °C to 700 °C, an obvious increase of methane conversion and aromatics yield could be observed, this happens due to

thermodynamic and kinetic effects. Nevertheless, if the temperature were too high, more carbonaceous deposits were formed, this might be disadvantageous to the catalytic efficiency of the catalyst.

Fig. 8 obviously shows that by increasing the temperature to 800 °C, methane conversion and aromatics yield quickly decreased. The high yield of coke, low yield of aromatics, too short life time and high energy ingesting are the limiting factors for this reaction at a high temperature. As could be seen, the best temperature for methane aromatization with 3%wt Mo/HZSM-5 catalysts is 700 °C [4,8,22].
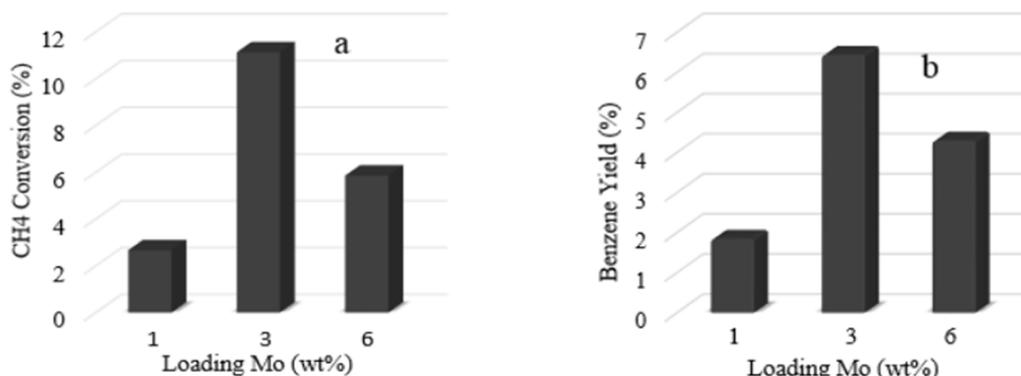
Fig. 7. a) Conversion of methane on different loads of Mo/HZSM-5 catalysts (T=700 °C, GHSV=2250 [mLg^{-1} h^{-1}], P=1 atm), b) Yield of benzene on different loads of Mo/HZSM-5 catalysts (T=700 °C, GHSV=2250 [mLg^{-1} h^{-1}], P=1 atm).
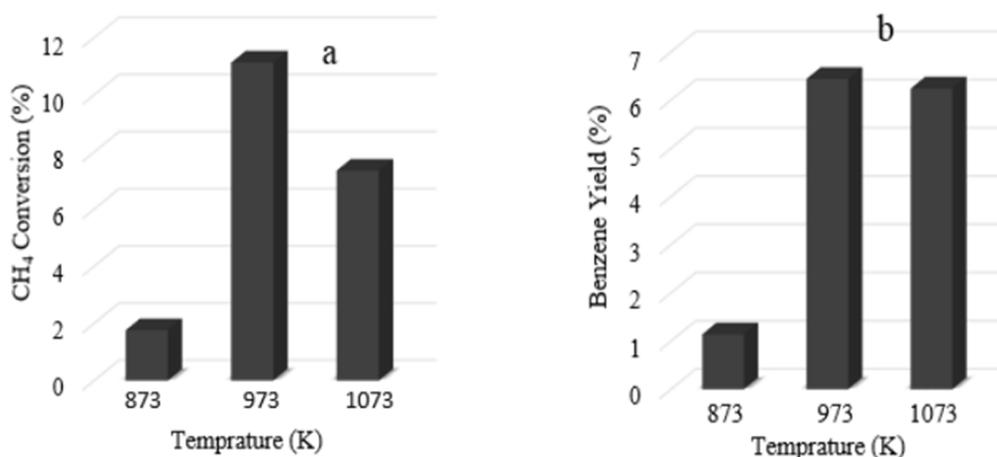
Fig. 8. a) Conversion of methane in different temperatures on 3%wt Mo/HZSM-5 catalysts (GHSV=2250 [mLg^{-1} h^{-1}], P=1 atm), b) Yield of benzene in different temperatures on 3%wt Mo/HZSM-5 catalysts (GHSV=2250 [mLg^{-1} h^{-1}], P=1 atm).

The comparison of methane conversion in different GHSVs (1500, 2250, 3600 [mLg^{-1}h^{-1}]) on 3%wt Mo/HZSM-5 is shown in Fig. 9a and the proportion of benzene yield of the reaction is shown in Fig. 9b. As can be seen, the best GHSV is 2250 [mLg^{-1} h^{-1}].

4. Conclusions

Different catalysts contained HZSM-5 and 3%Mo, 3%Zn, 3%Mn, 3%Cr, 3%Cd and 3%Ag/HZSM-5 impregnated and tested for methane dehydro-aromatization (MDA) reaction without oxidation conditions, the temperature was 973 K. Catalyst activities and catalysts selectivity were compared. The 3%Mo/ HZSM-5 catalyst showed a higher methane conversion, a higher benzene selectivity and a higher benzene yield, because Mo species due to the interaction with zeolite are well scattered in channels of zeolite and because of that, the 3% Mo/HZSM-5 has the highest value of selectivity. Different amount of Mo loaded HZSM-5 were compared and the proper loaded of Mo in Mo/HZSM-5 catalyst for the MDA reaction was 3wt%. Different temperatures and GHSVs were tested

for this reaction without the oxidative condition with 3%wt Mo/HZSM-5 catalyst and the best temperature and GHSV were 973K and 2250 [mLg^{-1}h^{-1}] respectively.

References

[1] A.V. Vosmerikov, V.I. Zaykovskii, L.L. Korobitsyna, E.G. Kodenev, V.V. Kozlov, G.V. Echevskii, Stud. Surf. Sci. Catal. 162 (2006) 913-920.
[2] Y. Shu, M. Ichikawa, Catal. Today 71 (2001) 55-67.
[3] J.H. Lunsford, Catal. Today 63 (2000) 165-174.
[4] K. Skutil, M. Taniewski, Fuel Process. Technol. 87 (2006) 511-521.
[5] D. Noon, B. Zohour, S. Senkan, J. Nat. Gas Sci. Eng. 18 (2014) 406-411.
[6] H.L. Mitchell III, R.H. Waghorne, U.S. Patent 4239658, 1980.
[7] S. Majhi, P. Mohanty, H. Wang, K. Pant, J. Energy Chem. 22 (2013) 543-554.
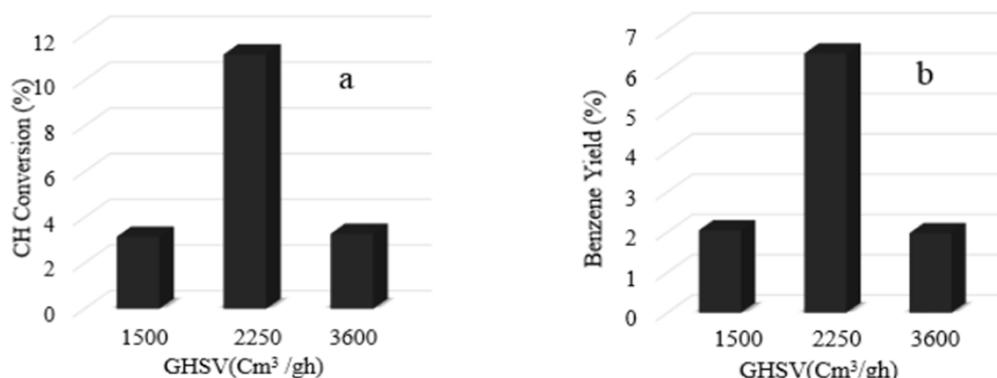
Fig. 9. a) Conversion of methane at different GHSVs on 3%wt Mo/HZSM-5 catalysts (T=700 °C, P=1 atm), b) Yield of benzene at different GHSVs on 3%wt Mo/HZSM-5 catalysts (T=700 °C, P=1 atm).

[8] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang, Y. Xu, Catal. Lett. 21 (1993) 35-41.

[9] S. Ma, X. Guo, L. Zhao, S. Scott, X. Bao, J. Energy Chem. 22 (2013) 1-20.

[10] Z. Yang, A. Kumar, A. Apblett, J Anal. Appl. Pyrol. 120 (2016) 484-492.

[11] J.-P. Tessonnier, B. Louis, S. Rigolet, M.J. Ledoux, C. Pham-Huu, Appl. Catal. A 336 (2008) 79-88.

[12] W. Liu, Y. Xu, J. Catal. 185 (1999) 386-392.

[13] H. Liu, W. Shen, X. Bao, Y. Xu, J. Mol. Catal. A: Chem. 244 (2006) 229-236.

[14] F. Solymosi, J. Cserényi, A. Szöke, T. Bánsági, A. Oszko, J. Catal. 165 (1997) 150-161.

[15] F. Solymosi, A. Erdöhelyi, A. Szöke, Catal. Lett. 32 (1995) 43-53.

[16] A. Szöke, F. Solymosi, Appl. Catal. A 142 (1996) 361-374.

[17] D. Wang, J.H. Lunsford, M.P. Rosynek, Top. Catal. 3 (1996) 289-297.

[18] D. Wang, J.H. Lunsford, M.P. Rosynek, J. Catal. 169 (1997) 347-358.

[19] S. Liu, L. Wang, R. Ohnishi, M. Ichikawa, J. Catal. 181 (1999) 175-188.

[20] M. Rahman, A. Sridhar, S.J. Khatib, Appl. Catal. A 558 (2018) 67-80.

[21] Y. Shu, D. Ma, L. Xu, Y. Xu, X. Bao, Catal. Lett. 70 (2000) 67-73.

[22] H. Liu, S. Yang, S. Wu, F. Shang, X. Yu, C. Xu, J. Guan, Q. Kan, Energy 36 (2011) 1582-1589.