

Methane Dehydroaromatization over Mo and W Catalysts Supported on ZSM-5

Zarei, Taleb; Davoodbeygi, Yegane*⁺

*Department of Chemical Engineering, University of Hormozgan, Bandar Abbas,
I.R. IRAN*

Islamimanesh, Saman

Lavan Oil Refinery Company, Lavan. I.R. IRAN

Zarei, Zahra

*Department of Chemical Engineering, Faculty of Engineering, Shahid Bahonar University of Kerman,
Kerman, I.R. IRAN*

ABSTRACT: Methane aromatization reaction to produce benzene using tungsten and molybdenum catalysts supported on ZSM-5 was investigated at 800 °C. Catalysts were prepared by impregnation of tungsten and molybdenum salts on ZSM-5 zeolite with various metal loadings in the range of 2-10 wt. %. In order to obtain the catalytic structures before and after the reaction, catalysts were characterized by XRD and FT-IR analysis. It was indicated from reactor tests that an increase in metal loading on the catalyst surface leads to an increase in methane conversion (1.1% and 3.2% for 2W/ZSM-5 and 6 W/ZSM-5, and 2.4% and 4.8% for 2Mo/ZSM-5 and 6 Mo/ZSM-5, respectively, at the time of stream, equals 120 min). It was also concluded that Mo catalysts show higher activity and stability than W (methane conversion of 3.2 and 9 % using 10Mo/ ZSM-5 and 10 W/ZSM-5 catalysts respectively, at the time of stream equals 100 min), and an increase of Mo loading leads to enhancement of catalytic activity and methane conversion, which indicates initial activation of methane has occurred on metal sites of catalysts. This activation leads to occur the later reactions and production of final benzene. These conditions confirm the two-factor mechanism which includes two stages: i) hemolysis break of C-H bond and CH₃ radical formation and then ethylene formation, and ii) cyclization of ethylene species in the presence of acidic sites within the zeolite channels. Investigations on mesoporous HMS support showed no aromatic production, which shows an increase in support channel diameter leads to reduce the possibility of ring formation.

KEYWORDS: Methane aromatization; ZSM-5 zeolite; Molybdenum; Tungsten; Cyclization.

INTRODUCTION

Methane, as the main component of natural gas, which is widely distributed around the world, has become

an important energy source in recent decades [1-4]. Methane can be used as the feed of processes for synthesizing

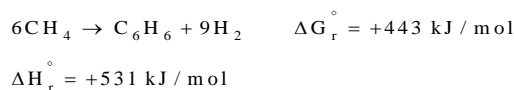
* To whom correspondence should be addressed.

+ E-mail: Y.davoodbeygi@hormozgan.ac.ir

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valuable product through two main routes of indirect and direct conversion [5, 6]. Indirect methane conversion involves methane reaction with water (i.e. steam reforming process) [7-9] or with oxygen (i.e. partial oxygen process) [10-12], to produce a mixture of hydrogen and carbon monoxide, which is called synthesis gas and used to form chemicals and fuels such as methanol, dimethyl ether, diesel fuel, and synthetic gasoline [5, 13, 14]. These processes need high temperatures and pressures and so they are energy intensive. The direct methane conversion to hydrogen and aromatics as a single-stage catalytic process is the second route for CH₄ conversion and has been an interesting topic for research. Oxidative dimerization to form ethane or ethylene, selective oxidation of methanol, and conversion with C₃ and C₄ hydrocarbons to produce aromatic hydrocarbons, are examples of direct methane conversion [2,15-17]. The presence of oxygen leads to the oxidation of produced hydrocarbons to CO₂ and H₂O which decreases the selectivity and makes the process expensive [5]. Oxygen-free aromatization process is considered an attractive alternative without any loss of hydrogen and carbon. Methane dehydroaromatization (MDA) is a non-oxidative process in which benzene is produced through the direct conversion of methane to benzene and hydrogen as the following reaction [18-25]:



Transition metals supported on high-silica zeolites have been introduced as appropriate catalysts in the MDA process [26-29]. Methane activation on metallic active sites, and cyclization (aromatization step) on acid sites of zeolite, are two rate-determining steps of the MDA process [30]. Molybdenum and tungsten are two active metals for MDA reactions. However, they suffer from coke formation on their active sites which leads to catalyst deactivation during MDA reaction. In fact stability of these catalysts is the main problem which is significantly reduced by methane decomposition and active site carbonization [30]. Direct conversion of methane to benzene was carried out for the first time by Wang *et al.* [31]. They synthesized Mo/HZSM-5 in the absence of oxygen and evaluated methane aromatization at 973 K in a fixed bed reactor and reported low conversion but with very high benzene selectivity. Lundsfore *et al.* [32] reported that Mo showed the highest methane conversion. Mo/HZSM-5 is reported

as a bifunctional catalyst. The carbonized Mo is an active phase for converting methane into ethylene, while the acid sites in HZSM-5 lead to ethylene conversion to aromatics such as benzene [24, 28, 33, and 34]. Zhang *et al.* [35] reported ZSM-5 zeolites with two-dimensional structure and channel diameter near benzene diameter are the best supports for MDA reaction. It is reported that, due to low methane reactivity, MDA reaction is commonly performed at above 600 °C. This reaction is limited by thermodynamic equilibrium. A temperature of 973 K is reported as the temperature which leads to a higher yield of benzene. However, this high temperature causes carbon deposition and rapid deactivation of the catalysts [29, 36]. On the other hand, highly resisted W-containing ZSM-5 samples were reported as the thermally stable catalyst, which has gained less attention [37-39]. According to the mentioned literature review, Mo and W metals supported on ZSM-5 were selected to be investigated in MDA process.

In this work, in order to investigate the role of Mo and W as active metals and ZSM-5 as support for MDA reaction, Mo and/or W catalysts supported on ZSM-5 zeolite have been synthesized via wet impregnation method, characterized by XRD, FT-IR and TPO analysis, and evaluated in MDA process. The effect of applied metal and its loading on the catalytic activity and methane conversion have been studied. Furthermore, the role of zeolite channel diameter has been also investigated.

EXPERIMENTAL SECTION

Chemicals

ZSM-5 zeolite (Si/Al=15) (ParsChemicalGroup, >99%), ammonium heptamolybdate (NH₄)₆Mo₇O₂₄ (Fluka, >98%), tungsten oxide (Sigma-Aldrich, 99.9%), tetraethyl orthosilicate (Sigma-Aldrich, 98%), hydrochloric acid (Merck, 37%), didecylamine (Sigma-Aldrich, 98%) and aluminum isopropoxide (Sigma-Aldrich, >98%) were used as the materials for catalysts synthesizing.

Catalysts preparation

Tungsten and molybdenum catalysts supported on ZSM-5

In order to synthesize W/ZSM-5 catalyst by the impregnation method, 1.365 g of tungsten oxide was dissolved in 100 mL of distilled water. 1 g ZSM-5 zeolite (Si/Al=15) was then added to the solution. The obtained

the mixture was stirred at 343 K for 6 h and after that, it was dried in the oven at 383 K for 24 h. Finally, in order to obtain tungsten oxide supported on ZSM-5 catalyst, the sample was calcined at 823 K for 6 h with a heating rate of 5 K/min. It should be noted that the active phase of catalyst for use in methane aromatization reaction is the metallic phase of the catalyst and in order to obtain this phase, the catalyst should be reduced to under 30 cc/min at 773 K for 2 h in the quartz reactor.

Mo/HZSM-5 catalyst was also prepared by a procedure similar to the one mentioned above for W/ZSM-5 catalyst. 1.1041 g of ammonium hepta-molybdate (Fluka, >99%) was impregnated on ZSM-5 zeolite. All steps of impregnating, drying, and calcination are similar to W/ZSM-5 catalysts. 2, 6, and 10 wt. % of Mo and W and also W-Mo bimetallic catalysts supported on ZSM-5 were synthesized and reduced. It should be mentioned that xY/ZSM-5 means that the catalyst contains "x" weight percent of "Y" metal, and the remaining is the support.

Preparation of mesoporous HMS zeolite

A mesoporous HMS with Si/Al ratio same as the zeolite (equal to 15) was synthesized in order to investigate the role of support in methane aromatization reaction. 15.0426 g of tetraethyl orthosilicate (TEOS) and 21.0033 g of ethanol were mixed and stirred for 30 min at room temperature (solution A). Furthermore, 1.4 mL of Hydrochloric acid (1N), 3.5 g dodecylamine, and 46 g water were mixed and stirred for 5 min at room temperature (solution B). A and B solutions were then mixed and the appropriate amount of aluminum isopropoxide was added the resulting solution was stirred for 6 h to produce a gel-like solution and kept for 18 h at room temperature. After that, the gel was filtered, washed with distilled water, and dried for 6 h at 100 °C. Finally, the dried precipitate was calcined for 6 h at 500 °C with a heating slope equal to 1.5 °C/min. Metals impregnation on the prepared mesoporous support was carried out in the same procedure as the ZSM-5-supported ones.

Catalyst characterization

XRD analysis was used to determine the crystalline structure of samples. The XRD patterns of catalysts were recorded on an X-ray diffractometer (PANalytical X'Pert-Pro) via a Cu-K α monochromatized radiation source and a Ni filter in the range $2\theta=4-80^\circ$

In order to determine the status of silanol groups (Si-OH) that exist on ZSM-5 zeolite and brosted sites, IR spectrum of catalysts before and after the reaction was evaluated by FT-IR analysis. Infrared spectra were recorded on a NEXus Fourier Transform InfraRed (FT-IR) spectrophotometer using KBr pellets containing a 1% weight sample in KBr.

In order to determine the state and type of carbon and coke deposited on catalysts, Temperature Programmed Oxidation (TPO) technique was applied. 100 mg of catalysts were heated from room temperature to 1073 K with 5 K/min heating rate under 30 mL/min N₂ stream containing 1% O₂ flow. Determination of CO₂ and CO contents was carried out by online gas chromatography.

Reactor system

1 g of catalyst is placed in a quartz reactor and was heated to reaction temperature. Fig. 1 shows a schematic of the catalytic test system and its various components. According to this figure, the system has the following components:

- 1- Hydrogen, methane, oxygen, and nitrogen cylinders for supplying required gas streams
- 2- Flow meter for setting the inlet gas velocity.
- 3- Cylinders containing silica gel to dry inlet gas to the reactor
- 4- Fixed-bed quartz reactor with 10 mm inner diameter and 10 cm height in which an appropriate amount of catalyst is placed.
- 5- Heating furnace (Lindberg) to supply the needed reaction temperature.
- 6- K-type thermocouple to measure the temperature of the heating furnace (reactor bed temperature)
- 7- Stainless steel pipes for online transferring of products to a Gas Chromatography (GC) device with a heating jacket to inhibit product condensation in a tube.
- 8- The GC device is connected to the reactor outlet and analyzes outlet gas, which is directly injected into the GC column by an injector valve of the gas sample. Outlet gas streams are analyzed during the reaction in optional time intervals.

A GC-6A Shimadzu (Japan) equipped with a heat conductivity detector and packed column with pure APK Q fixed phase with 1.5 m length and inner diameter of 1.8" was applied in order to identify and quantitative analysis of reaction products. The detector and column temperatures were set at 473 and 353 K, respectively, and

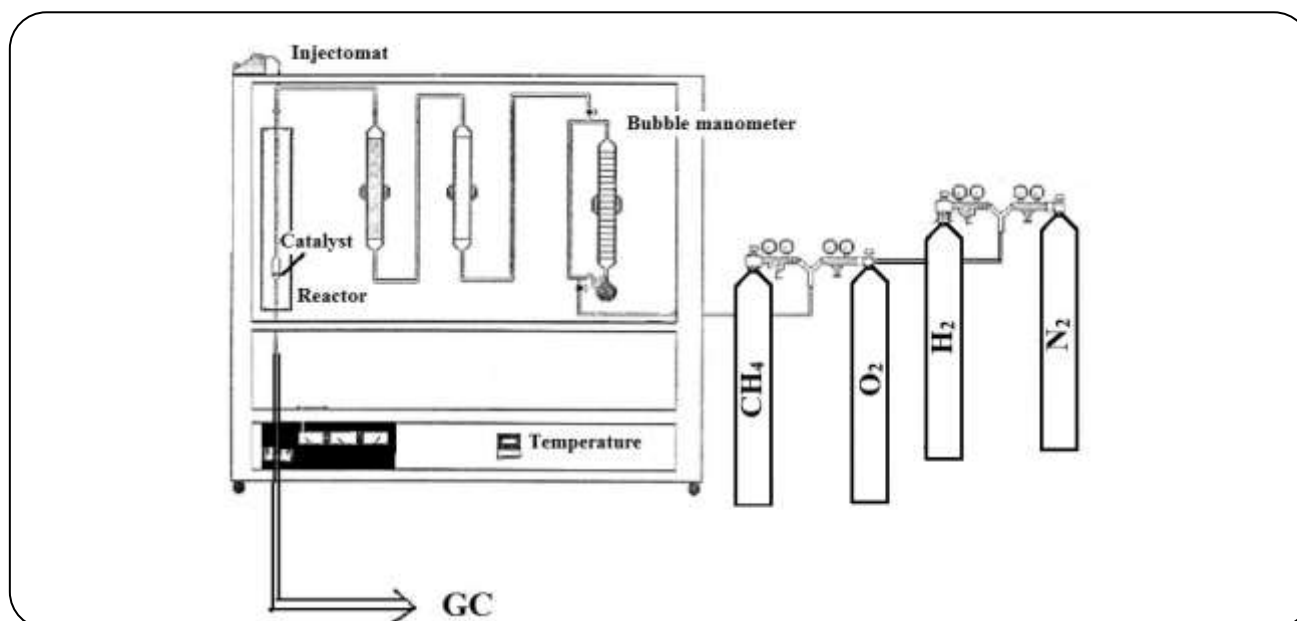


Fig. 1: Schematic of the catalytic test system.

carrier gas (helium) flow was set at 25 mL/min. The column temperature was increased from 353 to 453 K with 6 K/min heating rate.

Catalytic activity tests

The methane dehydroaromatization reaction (direct conversion of methane to benzene) is carried out according to the following procedure:

1 g of catalyst was placed in the fixed-bed quartz reactor. For catalyst degassing, 30 mL/min nitrogen stream passed over the catalysts and catalytic bed temperature were simultaneously increased to the desired value (973 to 1173 K) with 5 K/min heating rate. By reaching the desired temperature, the nitrogen stream was closed and the methane stream with GHSV equal to 15000 1/h was introduced to the reactor and passed through a catalyst bed and then reaction products were directly introduced to GC to be analyzed.

The chromatogram obtained from the MDA reaction on W/ZSM-5 is shown in Fig. 2.

Methane conversion and product selectivity are calculated using Equations (1) and (2), respectively as follows:

$$\text{Conversion (\%)} = \frac{\text{produced product}}{\text{amount of feed}} \times 100 \quad (1)$$

$$\text{Selectivity (\%)} = \frac{\text{amount of product 1}}{\text{amount of all products}} \times 100 \quad (2)$$

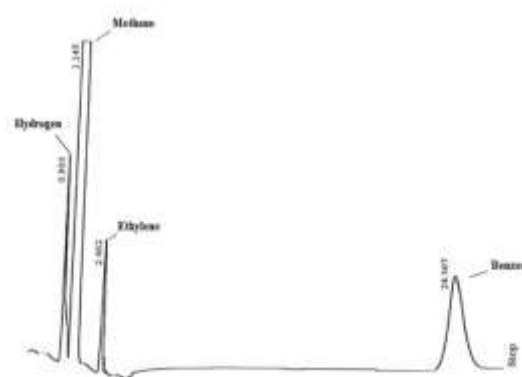


Fig. 2: A sample of GC chromatogram obtained from dehydroaromatization of methane.

RESULTS AND DISCUSSION

FT-IR analyses of the prepared catalysts before and after the reaction are shown in figures 3-a and 3-b, respectively. The absorption peak pattern of ZSM-5 is completely clear at 550, 850, 1100, 1225, 1400, 1650, and 3340 1/cm. The absorption peak at 550 1/cm corresponded to the symmetrical stretching vibration of a five-membered ring structure with T-O symmetry, and peaks at 1100 and 1225 1/cm correspond to internal and external asymmetrical stretching vibrations, respectively. The Bronsted acid peaks are between 36010 to 3630 1/cm. According to a decrease in intensity of peaks at 3425 and 3650 in the FT-IR spectrum of the used catalyst, a significant decrease of Bronsted sites of zeolite is deduced [40, 41].

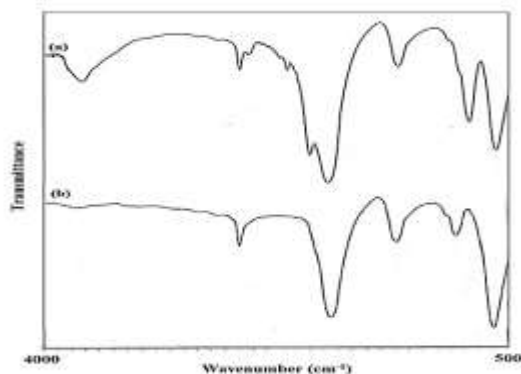


Fig. 3: FT-IR spectroscopy of ZSM-5, a) before the reaction, b) after the reaction.

XRD patterns of ZSM-5 zeolite before and after the reaction is shown in Fig. 4. Peaks at $2\theta = 7.89, 8.73, 14.82, 23.04, 23.86,$ and 24.26° corresponded to ZSM-5 zeolites which are illustrated in XRD patterns given in Fig. 4 [40]. As it is obvious in this figure, there is no significant difference both of wide and height of peaks of ZSM-5 before and after the reaction, so the crystalline structure of zeolite after the reaction is similar to the primary structure before the reaction which is because of ZSM-5 characteristics which have very high thermal stability. In fact, after the reaction which has been performed at 800°C , because of the similarity of XRD patterns with the fresh sample, it can be concluded that zeolite has acceptable thermal stability. The diameter of zeolite channels (5 \AA) [35, 42, 43] is the other advantage of ZSM-5 zeolite for this reaction which is approximately equal to the diameter of the benzene molecule and therefore it is suitable for MDA reaction.

Fig. 5 shows the performance of mono-metallic and bi-metallic catalysts supported on ZSM-5 with various metal loadings in MDA reaction. As can be seen in these figures, methane conversion to benzene increases by increasing metal loading on the catalyst surface. The methane conversions using 2, 6, and 10 wt. % of Mo on ZSM-5 are about 2.5, 5, and 9%, respectively. So it can be concluded that 10 wt. % of Mo is the best choice among the tested Mo/ZSM-5 samples. Results show higher activity and stability for Mo than W catalyst. Moreover, as it was mentioned above, methane conversion and catalytic activity are enhanced by increasing Mo loading. It can be concluded that the initial activation of methane occurs

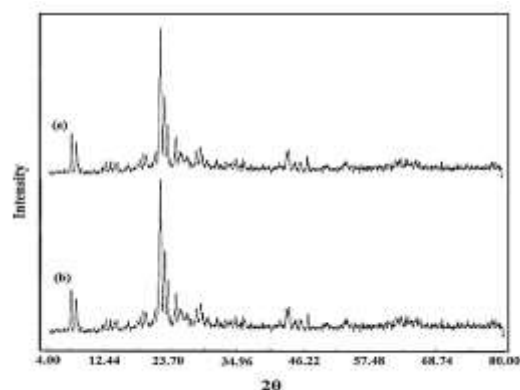


Fig. 4: XRD Patterns of ZSM-5, a) before the reaction, b) after the reaction.

on the metallic sites of the catalyst, and this activation leads to occur subsequent reactions and the final benzene production.

Fig. 6 shows catalysts selectivity for either ethylene, benzene, or naphthalene products. It is observed that ethylene production is occurring at the beginning of the reaction so the only product obtained during the first 30 minutes of the reaction is ethylene. This is seen in all experiments and no aromatic products are obtained during this time. Such a trend, which has been observed in other published articles [44-46] is a confirmation of the two functional mechanisms. This two-functional mechanism which was introduced by [32], contains two steps: I) hemolytic dissociation of the C-H bond, CH_3 formation, and then ethylene production, and II) cyclization of ethylene species in the presence of acidic sites in ZSM-5 channels. In fact, methane activation occurs on carbide species which results in ethylene formation as the primary product. The cyclization reaction is then carried out on acidic sites within the zeolite channels. Both catalysts showed high benzene selectivity (more than 85%) at all reaction conditions which is acceptable for this reaction.

Also, according to Figs. 6 and 7, catalysts show high benzene selectivity which is good for industrialization. It should be noted that as can be seen in these figures, naphthalene is produced in less than 10% of the reaction products. In order to confirm the presence of naphthalene and also investigate the probability of the presence of other aromatics, a trap was used in the reactor outlet and the effluent streams were cooled. It should be noted that

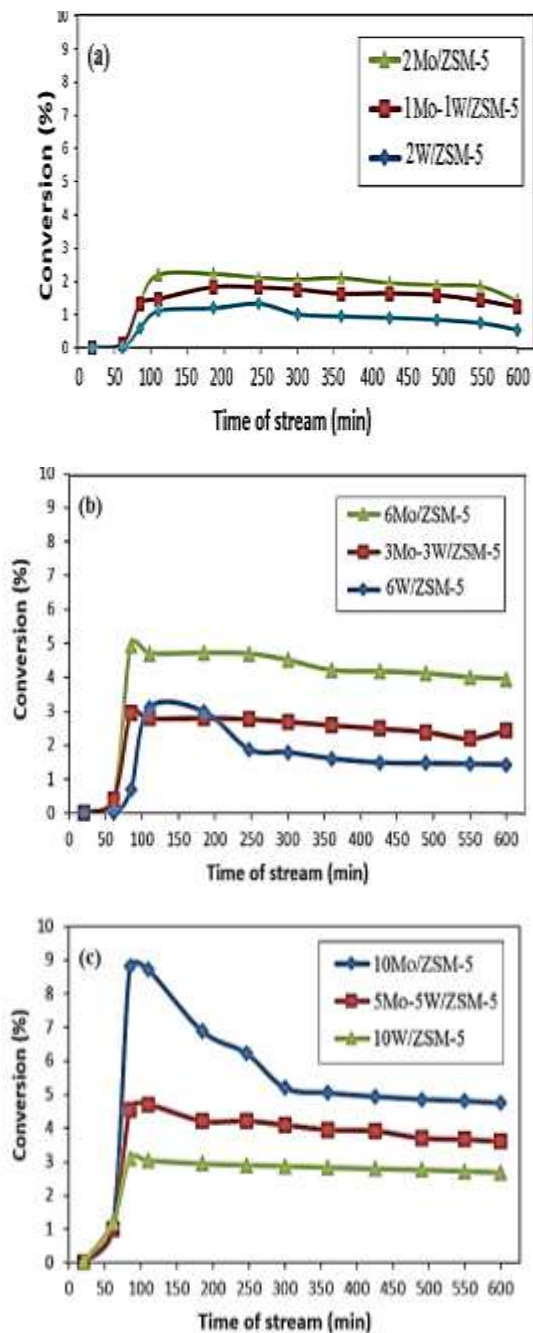


Fig. 5: Effect of metals (Mo and/or W) loadings (2, 6, and 10 wt.%) on methane conversion at 800 °C, atmospheric pressure, and GHSV=15000 1/hr.

in order to prevent benzene to be solidified, cooling was done at 40-50 °C. Finally, heavy products in solid form were collected and it was obtained that naphthalene was the only product in the collected sample. So it can be said with certainty that the only aromatic products produced from the reaction are benzene and naphthalene.

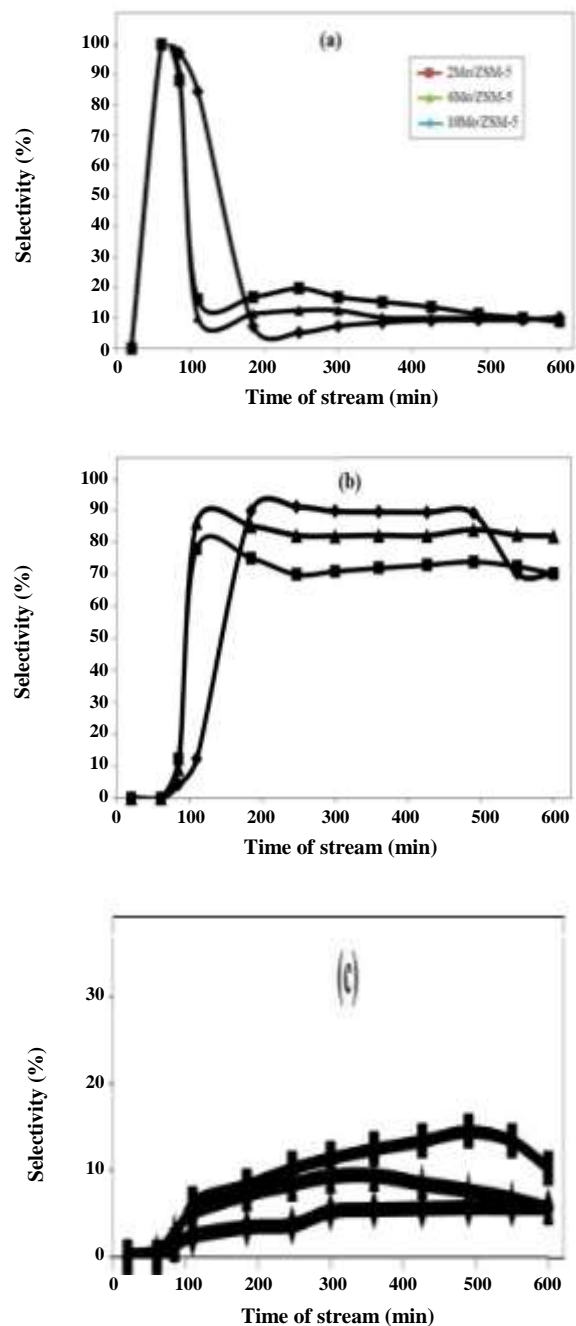


Fig. 6: Effect of Mo loadings on the selectivity of a) ethylene, b) benzene, and c) naphthalene at 800 °C, atmospheric pressure, and GHSV=15000 1/hr.

In order to study the effect of support on the catalytic performance, MDS reaction was also performed using 10Mo/mesoporous-ZSM-5 catalyst. Although the methane conversion was almost near to the conventional ZSM-5 support (which was discussed previously), the manner of the catalyst from the selectivities point of the view is completely different.

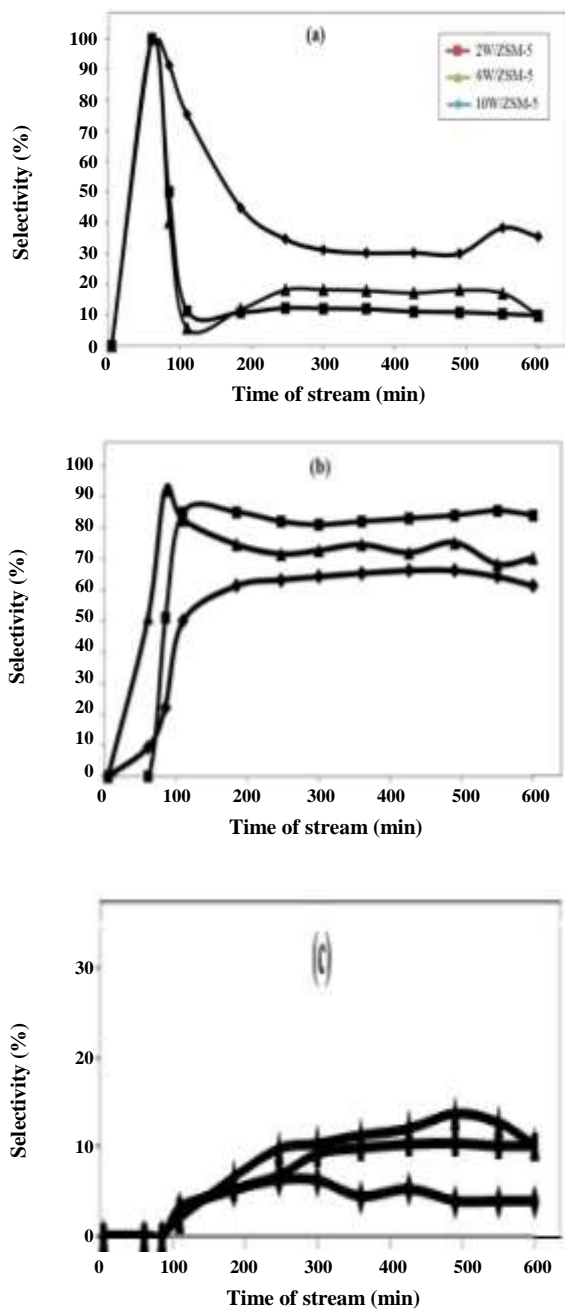


Fig. 7: Effect of W loadings on the selectivity of a) ethylene, b) benzene, and c) naphthalene at 800 °C, atmospheric pressure, and GHSV=15000 1/hr.

10Mo/mesoporous-ZSM-5 led to 8, 6, 4.5, 4.45, and 4.41% of methane conversion at 100, 200, 300, 500, and 600 °C, respectively, which are values near the commercial support. But on the other hand, the benzene selectivity is almost 0, and consequently, ethylene selectivity is up to 97%, at the whole range of temperatures. Results showed no formation

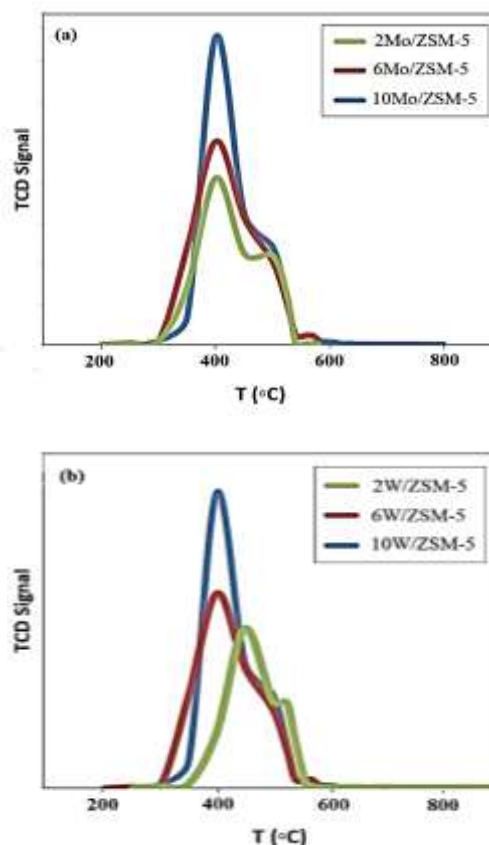


Fig. 8: TPO diagrams for different loadings of a) Mo and b) W supported on ZSM-5.

of aromatic products which indicates that the cyclization decrease by increasing the channel diameter of support.

TPO diagrams of used catalysts are shown in Fig. 8. A big and sharp peak is seen at 673 K which corresponds to the carbon on the metal supported on the external surface of ZSM-5. As it is obvious, the peak intensity is increased by increasing metal loading. Furthermore, a wide and small peak can be seen at 800 K which is corresponding to coke and polyaromatic deposited at bronsted sites of catalysts. The mentioned results indicate when the catalyst is pretreated (reduced) by hydrogen, less coke is formed in acidic sites. However, in W catalyst peak intensity is higher and there is a small peak at low temperature (573 K) which is corresponded to reversible removable coke which is deposited on metallic sites and leads to faster deactivation of W catalyst [47].

CONCLUSIONS

Methane aromatization reaction and its conversion to benzene using Mo and W catalysts supported on ZSM-5

were investigated. Results showed that an increase in metal loading on the surface of the catalyst leads to an increase in methane conversion to benzene and Mo catalysts have higher activity and stability, and higher Mo loading caused the enhancement of methane conversion and catalytic activity. In fact, the initial activation of methane on the catalysts occurs on the metallic sites of the catalyst. The best catalysts were 10Mo/ZSM-5 with 9% methane conversion and after that, the bimetallic composition of W and Mo showed 5% methane conversion at the first 100 minutes of the reaction. The amount of produced coke was similar in both catalysts and produced coke increased by increasing metal loading. However, if the reaction occurs in the presence of hydrogen, the possibility of coke formation decreases. Investigations of the pore diameter effect showed that an increase in support channel diameter leads to a decrease in ringing possibility. According to the benzene diameter (about 5 Å) it seems that the best support for benzene production in methane aromatization reaction is ZSM-5 zeolite.

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