Features of non-oxidative conversion of methane into aromatic hydrocarbons over Mo-containing zeolite catalysts

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Abstract. The results of study of methane conversion under non-oxidative conditions over molybdenum containing zeolite catalysts prepared by solid-phase synthesis using nanosized molybdenum powder are presented. The kinetic mechanisms of the process behavior under different conditions of methane dehydroaromatization are determined. It is shown that non-oxidative conversion of methane can occur both in the external diffusion and kinetic regions, depending on the methane flow rate. It is found out, that the optimum temperature of the methane conversion is 750 °C. It is shown that increased methane conversion is observed at the feed space velocity of methane decreasing from 1500 to 500 h⁻¹.

1. Introduction
Rational processing of hydrocarbon gases, whose main component is methane, is important in the petrochemical industry for production of valuable chemical products. Currently, most of these gases are used as fuel to produce heat and electricity or burned in flares at oil production sites. A most promising process for methane conversion is oxygen-free methane dehydroaromatization into aromatic hydrocarbons over zeolite catalysts modified with various transition metals. The possibility of methane conversion into aromatic hydrocarbons was shown in [1] in the 80-90-s. The conversion was performed in a pulsed mode at 740 °C over Pt- Zn-, and Ga/ZSM-5 catalysts. In 1993, Wang [2] proposed an effective molybdenum-containing zeolite catalyst based on HZSM-5. Anoxic conditions of this process provide a higher selectivity towards formation of aromatic hydrocarbons, while in the presence of oxygen the main reaction products are CO and CO₂.
From the viewpoint of thermodynamics, the non-oxidizing methane conversion (6CH₄↔9H₂ + C₆H₆) is not reasonable, because of the high power of C-H bond in a methane molecule (413 kJ/mol). However, despite the fact that ΔG = 0 only at 1075 °C in this reaction [3], significant amounts of benzene can already form at 700-800 °C [1].
Various metals – Mo, W, Fe, Cr, Mn, Pt, etc. and a large number of ZSM-5, ZSM-8, ZSM-11, HMCM-22, HMCM-41, TNU-9, and other zeolites have been investigated as the catalyst carriers for methane conversion [4]. Currently, the Mo/ZSM-5 catalyst is the most studied. A significant disadvantage is its rapid deactivation in the course of non-oxidative conversion of methane. In order to increase the stable performance of the catalyst, use is made of modification of the support surface, addition of promoters and small amounts of oxidants, and changes in the number and strength of the zeolite acid sites by varying the silica modulus [5]. Mo/ZSM-5 catalysts are generally prepared by impregnating of zeolite with an aqueous solution of (NH₄)₆Mo₇O₂₄ • 4H₂O [6]. Also, Mo-containing catalysts are prepared by solid-phase synthesis and by mixing the zeolite with a molybdenum oxide or
molybdenum salts. It is shown that the catalysts prepared by solid phase synthesis could be either less or more active in the course of conversion of methane into aromatic hydrocarbons compared to the catalysts manufactured by impregnation. Differences in the activity of Mo/ZSM-5 catalysts prepared by different methods are due to different localization of molybdenum on the zeolite surface [7]. In [8], the authors reported the use of nanosized molybdenum powder to prepare Mo/ZSM-5 catalyst characterized by improved activity and stability compared to those prepared by impregnation or mechanical mixing of the zeolite with a molybdenum oxide or salt.

It is known that Mo/ZSM-5 catalysts are bifunctional [4,8], in the cases where methane is activated on the active sites of molybdenum to form ethylene – the initial reaction product, while its further oligomerization and aromatization occur on the acid sites of the zeolite to form benzene and naphthalene.

It has been found out that Mo2C is an active site of methane activation [4,9], which is formed during the induction period. However, the excessive formation of coke on the catalyst active sites results in its lower activity and stable operation in the course of non-oxidative conversion of methane into aromatic hydrocarbons.

The aim of this work is to study the effect of the conditions of methane conversion in the presence of Mo/ZSM-5 catalyst, prepared by solid-phase synthesis using nanosized Mo powder, on composition and yield of the resulting products.

2. Experimental
A zeolite with SiO$_2$/Al$_2$O$_3$ = 40 was prepared via hydrothermal synthesis using hexamethylenediamine as a template. The degree of crystallinity of the resulting zeolite was 100%. A molybdenum-containing catalyst was prepared via solid-phase synthesis by mechanical mixing of HZSM-5 zeolite with a nanosized powder of molybdenum (Mo NSP) in a vibratory ball mill for 2 hours. The resulting mixture was calcinated at 540 °C for 4 hours in air. The Mo NSP was prepared by the method of electric wire explosion in argon atmosphere (average particle size 70-100 nm) [10]. The content of molybdenum in the catalyst was 4.0 wt%.

The process of methane conversion was conducted in a laboratory flow-type quartz reactor at atmospheric pressure, the reaction temperature 600-750 °C and the feed space velocity of methane from 500 to 1500 h$^{-1}$. A 0.5-2.0 cm$^3$ volume of the catalyst (particle size 0.5-1.0 mm) was placed on the quartz reactor lattice to heat in a helium stream to the reaction temperature and maintained at this temperature for 10 min, the supply of helium to reactor was then stopped and methane (purity 99.9 %) was let in. The reaction products (ethane, ethylene, benzene, toluene, and naphthalene) were analyzed by gas chromatography. In order to estimate the catalytic activity of the samples, the degree of propane conversion was estimated. The yield and selectivity towards the formation of the gaseous and liquid products were also calculated.

3. Results and Discussion
To determine the optimal conditions for non-oxidative methane conversion, the effect of temperature and feed space velocity of methane was investigated.

Figure 1 presents the data on the yield of aromatic hydrocarbons versus the methane flow rate at different contact times. These data show that the kinetic curves of the yield in methane conversion products on the flow rate for different contact times are similar. When the flow of methane increases, the yield in aromatic hydrocarbons also increases to a certain value, after which the arene yield remains practically unchanged. This indicates that in the cases where little methane is consumed, the process runs in the external diffusion region, while as the methane flow rate increases the conversion occurs in the kinetic region. We observed that in the latter case different methane flow rates correspond to different contact times.
Figure 1. Yield in aromatic products of methane conversion vs the methane flow rate for contact times: 7.2 s (a), 3.6 s (b), and 2.4 s (c).
Thus, when the contact time is reduced from 7.2 to 2.4 s, the transition into the kinetic region is observed at higher methane flow values. Therefore, in further experiments we selected the methane flow rates to rule out the external diffusion inhibition and to make the process run in the kinetic region.

The data on the effect of reaction temperature on the yield and selectivity towards formation of aromatic hydrocarbons are shown in Table 1.

Table 1. Effect of temperature on the process of methane conversion over Mo/ZSM-5 catalyst (contact time 3.6 s).

| Temperature, °C | Benzene, % | Toluene, % | Naphtalene, % | Selectivity towards arenes, % | Conversion of methane, % |
|----------------|------------|------------|---------------|-----------------------------|-------------------------|
| 600            | 0.07       | 0.01       | 0.26          | 78.7                        | 0.3                     |
| 650            | 1.40       | 0.04       | 1.06          | 80.3                        | 2.4                     |
| 700            | 5.79       | 0.09       | 2.31          | 79.7                        | 7.8                     |
| 750            | 10.48      | 0.21       | 4.90          | 79.8                        | 15.2                    |

They show that an increase in the reaction temperature from 600 to 750 °C results in an increase in the methane conversion from 0.3 to 15.2%, which also increases the product yield. For instance, the benzene yield increased from 0.07 to 10.48% due to an increase in the reaction temperature to 750 °C, while selectivity towards formation of aromatic hydrocarbons is practically unchanged and remains at the level of 79-80%. This seems to be due to the thermodynamic characteristics of the process, wherein the increase in the reaction temperature favors the highest rate of selective conversion of methane into aromatic hydrocarbons. The increase in the reaction temperature to 800-850 °C results in a transient increase in methane conversion at the beginning of the process but then the catalyst activity decreases sharply due to an increased surface coking.

The data on the changes in the activity of Mo-containing zeolite catalyst are shown in Figure 2 versus the time of the process for the methane feed space velocity 500-1500 h\(^{-1}\).

![Figure 2](image_url). Dependence of methane conversion on the reaction time for methane feed space velocity 500-1500 h\(^{-1}\).

It is evident from Figure 2 that a decrease in the methane feed space velocity results in an increased methane conversion. However, the conversion of methane at the space velocity 500 h\(^{-1}\) is lower.
(11.6%) within the first 20 minutes of the reaction at 1000 h\(^{-1}\) (15.2%) and 1500 h\(^{-1}\) (15.4%), which is due to a longer induction period at low methane feed space velocities. An increase in a space velocity to 1500 h\(^{-1}\) results in a sharper decrease in the methane conversion and shorter period of stable performance of the catalyst as a result of caused by increased catalyst loading and formation of large amounts of carbonaceous deposits with a high degree of condensation.

Figure 3 shows the yields of basic products of non-oxidative conversion of methane versus the reaction time. An analysis of the gaseous products of non-oxidative methane conversion over Mo/ZSM-5 catalyst demonstrated that the major products are ethylene and ethane. For all feed space velocities of methane under study the yield in ethane is less than 0.16%. It is known that ethylene is the primary product of non-oxidative methane conversion, which is oligomerized on Bronsted acid sites of the zeolite to benzene and naphthalene. Therefore, the lowest \(\text{C}_2\text{H}_4\) concentration is observed within the first minutes of the reaction. During the reaction of methane dehydroaromatization, the active and acid zeolite sites carbonize, giving lower benzene and naphthalene yields, hence an increase in concentration of ethylene.

The liquid products of methane conversion contain benzene and naphthalene. The fraction of benzene is higher than that of naphthalene. For all feed space velocities of methane under study the highest amount of benzene is formed within the first 20-60 minutes of the reaction, after which the concentration is gradually reduced due to catalyst carbonization. The maximum yield in benzene in the first 20 minutes of the reaction was 7% at feed space velocity of methane under study 1500 h\(^{-1}\). This is due to the fact that at high space velocities, the induction period is shorter. The highest amount of naphthalene is produced at the beginning of dehydroaromatization reaction at the feed space velocity of methane 1000 h\(^{-1}\). As the reaction runs, the yield in naphthalene decreases for all feed space velocities of methane.

**Figure 3.** The yield in ethane (a), ethylene (b), benzene (c) and naphthalene (d) over Mo/ZSM-5 catalyst in the course of non-oxidative methane conversion.
Based on the experimental data obtained and available information on conversion of hydrocarbons over ZSM-5 zeolites [9,11], in Table 2 we summarize the chemical reactions representing the basic patterns of non-oxidative methane conversion.

| Reaction       | Product          | Reaction       | Product          |
|----------------|------------------|----------------|------------------|
| $2\text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + 3\text{H}_2$ | acetylene | $2\text{C}_6\text{H}_6 \rightarrow \text{C}_{10}\text{H}_8 + \text{C}_2\text{H}_4$ | naphthalene |
| $2\text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2$ | ethylene | $\text{C}_{10}\text{H}_8 + \text{C}_2\text{H}_6 \rightarrow \text{C}_{12}\text{H}_{12} + \text{H}_2$ | methyl naphthalene |
| $2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2$ | ethane | $\text{C}_6\text{H}_6 + \text{CH}_4 \rightarrow \text{C}_7\text{H}_8 + \text{H}_2$ | toluene |
| $6\text{CH}_4 \rightarrow \text{C}_6\text{H}_6 + 9\text{H}_2$ | benzene | $\text{C}_7\text{H}_8 + \text{CH}_4 \rightarrow \text{C}_{12}\text{H}_{12} + \text{H}_2$ | dimethyl naphthalene |
| $3\text{C}_2\text{H}_6 \rightarrow \text{C}_6\text{H}_6 + \text{H}_2$ | benzene | $\text{C}_2\text{H}_4 \rightarrow \text{C} + 2\text{H}_2$ | coke |
| $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$ | ethylene | $\text{C}_6\text{H}_6 \rightarrow \text{C}_7\text{H}_8 + \text{H}_2$ | toluene |

4. Conclusion

The process of non-oxidative conversion of methane over Mo/ZSM-5 catalysts prepared via solid phase synthesis using nanosized molybdenum powder has been investigated. The kinetic mechanisms of methane conversion have been studied and optimal conditions have been identified. It has been shown that the optimum temperature of non-oxidative methane conversion, at which the conversion efficiency is the highest and so is the selectivity towards benzene formation (15.2 and 10.48%, respectively), is 750 °C at the methane feed space velocity 1000 h⁻¹.

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