# Nonoxidative Conversion of Methane to Aromatic Hydrocarbons in the Presence of ZSM-5 Zeolites Modified with Molybdenum and Rhenium

A. A. Stepanov<sup>a</sup>, V. I. Zaikovskii<sup>b, c</sup>, L. L. Korobitsyna<sup>a</sup>, and A. V. Vosmerikov<sup>a, \*</sup>

<sup>a</sup>Institute of Petroleum Chemistry, Siberian Branch, Russian Academy of Sciences, Tomsk, Russia <sup>b</sup>Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia <sup>c</sup>Novosibirsk National Research State University, Novosibirsk, Russia \*e-mail: pika@ipc.tsc.ru

Received April 17, 2018; Revised May 21, 2018; Accepted July 26, 2018

**Abstract**—The nonoxidative conversion of methane to aromatic hydrocarbons in the presence of a high-silica ZSM-5 zeolite modified with molybdenum and rhenium nanopowders has been studied. Data on the acid characteristics of the catalysts have been derived by temperature-programmed desorption of ammonia. The microstructure and composition of the Re/ZSM-5 and Re–Mo/ZSM-5 catalyst systems have been studied by transmission electron microscopy. It has been shown that modification of a Mo-containing zeolite with rhenium leads to an increase in the activity and stability of the catalyst in the methane dehydroaromatization reaction.

**Keywords:** methane, aromatic hydrocarbons, natural gas, zeolite, molybdenum and rhenium nanopowders **DOI:** 10.1134/S0965544119010146

The development of processes for converting natural and associated petroleum gases to valuable chemical products, instead of gas flaring at fields, will provide not only a decrease in the negative environmental impact, but also the prevention of a loss of valuable hydrocarbon feedstocks in which the main component is methane. Of greatest interest is the nonoxidative conversion of methane to aromatic hydrocarbons in the presence of zeolite catalysts modified with transition metal ions; with respect to activity in this process, the metals can be arranged in the following order: Mo > W > Fe > V > Cr [1]. Wang et al. [2] studied the methane conversion process in the presence of Re/ZSM-5 catalysts synthesized by impregnating the zeolite with an  $(NH_4)_2 ReO_4 \cdot 4H_2O$  aqueous solution and subsequently calcining the samples at 500°C. It was reported that the activity of Re-containing zeolites in the methane dehydroaromatization reaction is comparable with the activity of Mo/ZSM-5 catalysts. With respect to a number of physical properties, rhenium approaches group VI refractory metals (molybdenum, tungsten) and platinum group metals. With respect to the melting point, rhenium ranks second among metals, being inferior only to tungsten. It is the basic component in the production of catalysts for petroleum refining processes, for example, rheniumplatinum catalysts used to produce a high-octane gasoline component. The main problem of catalysts for

deactivation in the process. To increase the activity and stable on-stream time, the catalysts are modified with various metals, such as La, Pt, V, Fe, Zn, Co, and Ni [3–6]. This paper describes results of studying the nonoxidative conversion of methane to aromatic hydrocar-

the nonoxidative conversion of methane is their rapid

idative conversion of methane to aromatic hydrocarbons in the presence of Re/ZSM-5 and Re– Mo/ZSM-5 catalysts prepared by solid-phase synthesis using Mo and Re nanopowders (NPs).

#### **EXPERIMENTAL**

The Re/ZSM-5 and Mo/ZSM-5 catalysts were prepared by solid-phase synthesis by dry mechanical mixing of the ZSM-5 zeolite in the H-form  $(SiO_2/Al_2O_3 \text{ molar ratio of 40})$  and Mo and Re NPs in a KM-1 vibratory ball mill (German Democratic Republic) for 2 h. The Mo and Re NPs were prepared by an electric explosion of respective wires in an argon atmosphere. The average particle size of Mo and Re was 70 and 150 nm, respectively. The resulting mixture was calcined at a temperature of 540°C for 4 h. The Mo and Re content in the zeolite was 4.0 and 5.0 wt %, respectively. The Re–Mo/ZSM-5 catalysts were synthesized by adding the Re NP to the 4.0%Mo/ZSM-5 sample and subsequently stirring the resulting mixture in a vibratory mill for 2 h. The rhenium content in the



Fig. 1. Powder diffraction patterns of : (1) ZSM-5, (2) the Re NP, and (3) 5.0%Re/ZSM-5 samples before the reaction, and (4) 5.0%Re/ZSM-5 after the reaction.

Re–Mo/ZSM-5 catalyst was varied in a range of 0.1– 5.0 wt %.

X-ray diffraction analysis was conducted on a Bruker DISCOVER D8 diffractometer using monochromatic Cu $K_{\alpha}$  radiation and a Lynx-Eye detector. Scanning was conducted in an angular range of  $2\theta = 5^{\circ}-88^{\circ}$  in increments of 0.02 deg at an acquisition time of 3 s per point.

The specific surface area of the catalysts was measured by low-temperature nitrogen adsorption on a Micromeritics ASAP 2020 instrument (the United States). The calculation of the specific surface area of the test sample was conducted by a multipoint BET method.

The acid characteristics of the samples were studied by temperature-programmed desorption of ammonia; this method makes it possible to determine the strength distribution of acid sites and their concentration. The acid site concentration in the catalysts was determined from the amount of ammonia desorbed at the time of recording of the desorption peaks and expressed in terms of micromoles per gram of catalyst.

The structure of the Re/ZSM-5 and Re– Mo/ZSM-5 catalysts was studied by high-resolution transmission electron microscopy (HR-TEM) in a scanning mode using the Z-contrast imaging (highangle annular dark-field scanning transmission electron microscopy (HAADF-STEM)) [7]. The studies were conducted on a JEM-2200FS atomic-resolution electron microscope.

The nonoxidative conversion of methane was run on a laboratory flow system at atmospheric pressure and a temperature of 750°C. A catalyst sample with a particle size of 0.5-1.0 mm was placed into a tubular quartz reactor with a diameter of 12 mm; the volume of the catalyst loaded in the reactor was 1 cm<sup>3</sup>. Before reaction, the catalyst was heated in a helium stream to 750°C and held at this temperature for 10 min; after that, the supply of helium was ceased; instead, methane (purity of 99.99 vol %) was fed at a space velocity of 1000 h<sup>-1</sup>. Every 40 min of the process, the reaction products were analyzed by gas—liquid chromatography on a Chromatec Kristall-5000.2 chromatograph. To determine the catalytic activity of the samples, the methane conversion and the product yield were determined.

#### **RESULTS AND DISCUSSION**

Figure 1 shows powder diffraction patterns of the ZSM-5 zeolite, the Re NP, and the 5.0%Re/ZSM-5 catalyst samples before and after the nonoxidative conversion of methane. It is evident that the patterns of the two 5.0%Re/ZSM-5 catalyst samples exhibit peaks at 37.613°, 40.454°, 42.895°, 56.394°, 67.819°, 75.259°, 81.997°, and 83.659°, which are characteristic of metallic Re (PDF 01-089-2935); the presence of rhenium oxide phases in the catalyst is not observed.

Results of studying the activity of the 4.0%Mo/ZSM-5 and 5.0%Re/ZSM-5 catalysts and Re-4.0%Mo/ZSM-5 samples containing different amounts of rhenium in the methane dehydroaromatization reaction are shown in Fig. 2. It is evident that the activity of the 5.0%Re/ZSM-5 catalyst is significantly lower than that of the 4.0%Mo/ZSM-5 sample. In a 20-min reaction in the presence of the 5.0%Re/ZSM-5 catalysts, the maximum methane conversion is 3.6 and 13.5%, respectively. With an increase in the presence of either of the catalysts.



**Fig. 2.** Variation in methane conversion in the presence of Re–4.0% Mo/ZSM-5 catalysts containing different amounts of rhenium: (1) 0, (2) 0.1, (3) 0.5, (4) 0.7, (5) 1.0, and (6) 2.0 wt % and (7) the 5.0% Re/ZSM-5 catalyst as a function of on-stream time.

An increase in the Re NP content in the 4.0%Mo/ZSM-5 catalyst leads to an increase in the catalyst activity in the methane conversion process. Thus, within 20 min of reaction in the presence of the 0.5%Re-4.0%MoZSM-5 catalyst, the methane conversion achieves 14.8% versus 13.5% provided by the 4.0%MoZSM-5 sample. A further increase in the Re concentration in the 4.0%Mo/ZSM-5 catalyst leads to a decrease in the catalyst activity in methane conversion. Within the first 20 min of reaction in the presence of the 2.0%Re-4.0%Mo/ZSM-5 catalyst, the methane conversion achieves 11.9%. For all the studied Re-Mo/ZSM catalysts, the methane conversion decreases with increasing process time.

Analysis of the composition of the gaseous methane conversion products formed in the presence of zeolites containing Re and Mo showed that the total yield of ethane and ethylene gradually increases during the reaction; after 180–260 min the process, it decreases because of the coking of the active sites of the catalysts (Fig. 3a). The highest amount of ethane and ethylene–1.2%—is formed in the presence of the 2.0%Re–4.0%Mo/ZSM-5 catalyst. However, after 220 min of reaction, the total yield of ethane and ethylene abruptly decreases; after 300 min on stream, the yield provided by this catalyst is lower than the yield observed for the other samples. The lowest amount of ethane and ethylene is formed in the presence of the 5.0%Re/ZSM-5 catalyst; it does not exceed 0.6%.

Analysis of the liquid products of methane conversion showed that they mostly contain benzene and naphthalene (Figs. 3b, 3c). The highest amount of benzene (7.5%) is formed in the presence of the Mo/ZSM-5 catalyst containing 0.5% Re within the first 20 min of reaction (Fig. 3b). In the presence of the 1.0%Re-4.0%Mo/ZSM-5 sample, the benzene yield decreases compared with the yield provided by



**Fig. 3.** Total yield of (a) ethane and ethylene, (b) benzene, and (c) naphthalene in the presence of the Re–4.0%Mo/ZSM-5 samples containing different amounts of Re: (1) 0, (2) 0.5, and (3) 2.0% and (4) the 5.0%Re/ZSM-5 catalyst as a function of on-stream time

the 4.0%Mo/ZSM-5 catalyst. The lowest amount of benzene (1.8%) within 20 min of reaction is formed over the 5.0%Re/ZSM-5 catalyst. During methane dehydroaromatization, the benzene yield decreases in the presence of all the catalysts.

The addition of 0.5% rhenium to the 4.0% Mo/ZSM-5 catalyst leads to a 0.4% increase in the naphthalene yield; after 100 min of reaction, the naphthalene yield abruptly decreases in the presence of either of the catalysts (Fig. 3c). The other samples provide the formation of a significantly lower amount

Catalyst	Temperature, °C		Concentration, µmol/g			$\mathbf{S} = m^2/\sigma$
	$T_{\mathrm{I}}$	$T_{\rm II}$	CI	$C_{\mathrm{II}}$	$C_{\Sigma}$	$S_{sp}, m^{-}/g$
ZSM-5	201	435	710	286	996	377
4.0%Mo/ZSM-5	200	415	694	234	928	315
5.0%Re/ZSM-5	190	420	602	287	889	395
0.5%Re-4.0%Mo/ZSM-5	190	395	671	214	885	330
1.0%Re-4.0%Mo/ZSM-5	185	390	658	193	851	337
2.0%Re-4.0%Mo/ZSM-5	180	385	637	170	807	358

Table 1. Acid characteristics and specific surface area of the catalysts

 $T_{\rm I}$  and  $T_{\rm II}$  are the temperatures of the low- and high-temperature peak maxima in the thermal desorption curves;  $C_{\rm I}$ ,  $C_{\rm II}$ , and  $C_{\Sigma}$  are the concentrations of weak and strong acid sites and their sum, respectively.

of naphthalene both at the beginning of the process and during the reaction.

Thus, the additional introduction of Re into the Mo-containing zeolite does not lead to a change in the qualitative composition of the liquid products of methane conversion; it provides an increase in the yield of these products. The highest activity and stability in the nonoxidative conversion of methane is exhibited by the 0.5%Re-4.0%Mo/ZSM-5 catalyst. The increase in the catalyst activity is attributed to the unique properties of rhenium, which performs both the dehydrogenating and hydrogenating functions; this feature provides a decrease in the coking rate [8]. In addition, rhenium does not undergo recrystallization during catalysis because it has a high melting point [9].

Since catalysts for the nonoxidative conversion of methane have a bifunctional nature of action [10-12], which is associated with the involvement of both the metal active sites and the Brønsted acid sites of the zeolite, it was of interest to study the acid properties of the ZSM-5 zeolite and the zeolite samples modified with molybdenum and rhenium.

Results of studying the acid properties of the catalysts are shown in Table 1. It is evident that the ZSM-5 zeolite is characterized by the highest concentration of strong acid sites. The addition of the Mo NP to the zeolite leads to a decrease in the strength and concentration of the acid sites of the catalyst: the total number of acid sites decreases from 996 to 928  $\mu$ mol/g, while the concentration of strong acid sites decreases from 286 to 234  $\mu$ mol/g. The observed changes in the acid properties of the Mo/ZSM-5 catalyst are attributed to the fact that, during the calcina-

tion of the catalyst in air at  $540^{\circ}$ C, molybdenum compounds are partially localized on the outer zeolite surface and some of the compounds migrate to the zeolite channels, where they interact with the acid sites [13]. At high calcination temperatures, the zeolite matrix can undergo dealumination to form aluminum molybdate Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>, which leads to the degradation of the crystal lattice of the zeolite [14]. Thus, during the catalyst synthesis, the state of both the molybdenum and the zeolite matrix undergoes changes. In addition, the patterns of change in the acid properties of the zeolite upon the introduction of rhenium and molybdenum are different.

For the 5.0% Re/ZSM-5 catalyst, the concentration of low-temperature acid sites located mostly on the outer zeolite surface decreases, while the content of high-temperature acid sites located in the zeolite channels does not change. This finding is attributed to the fact that, at high calcination temperatures of the catalyst, rhenium nanoparticles undergo aggregation into large entities that block the zeolite channels. At the same time, rhenium does not migrate to the zeolite channels and does not interact with strong acid sites [15]. The addition of rhenium to the 4.0% Mo/ZSM-5 catalyst leads to a decrease in the acid site concentration in the sample. With an increase in the Re content in the catalyst from 0.5 to 2.0%, the concentration of strong acid sites decreases from 214 to 170  $\mu$ mol/g; the concentration of weak acid sites also significantly decreases. It should be noted that the Re-Mo/ZSM-5 catalysts, after adding Re NP to Mo/ZSM-5 and mixing in a vibratory mill, were not calcined prior to studies by temperature-programmed desorption of ammonia. The observed decrease in the



Fig. 4. High-angle annular dark-field STEM image of the 5.0% Re/ZSM-5 catalyst before reaction.

catalyst acidity is apparently associated with the blocking of the active sites by rhenium both in the zeolite channels and on the zeolite surface during the catalyst synthesis. In the case of calcination of the Re/ZSM-5 catalyst, large rhenium oxide particles are formed; they do not penetrate into the zeolite channels, and the concentration of strong acid sites does not change [15].

Results of studying the specific surface area of the Re/ZSM-5 and Re–Mo/ZSM-5 catalysts showed that all the samples have a high specific surface area, which increases with an increase in the Re content in the catalyst (Table 1). Thus, an increase in the Re concentration from 0.5 to 2.0% in the Re–Mo/ZSM-5 catalyst leads to an increase in the specific surface area from 330 to 358 m<sup>2</sup>/g.

Electron microscopic studies showed that the 5.0%Re/ZSM-5 catalyst contains a small amount of Re particles with a size of up to 10 nm; the dominant state of rhenium is aggregated clusters of particles with a particle size of about 2 nm and a cluster size of 10-30 nm. Along with aggregates, individual Re clusters with a size of about 2 nm are present (Fig. 4, marked with arrow 1). Some of the clusters have the form of sticks (2) with shape anisotropy:  $I \times d = (2-3) \times (5-$ 100) nm. An ordered arrangement of clusters with a periodicity of 2.5 nm is observed (3); sometimes, the periodicity is  $\approx 4.5$  nm (4). In some cases, branched sticks are observed (5). It can be assumed that individual clusters and sticks are localized in the zeolite channels; their spreading takes place; however, they spread no farther than to two adjacent zeolite channels.

After 380 min on stream in the nonoxidative conversion of methane, the 5.0% Re/ZSM-5 catalyst contains Re particles differing in size and morphology (Fig. 5). It is evident that rhenium emerges to the sur-

face and undergoes agglomeration into large surface particles.

Figure 5a shows Re particles with a size of 15–20 nm. A carbon layer with a graphite structure and a thickness of  $\approx 2$  nm is present on the zeolite surface (Fig. 5b). The HRTEM image of an individual large Re particle (size of  $\approx 20$  nm) on zeolite shows that the Re surface is covered with a carbon layer with a graphite structure ( $d_{002} = 0.35$  nm) and a thickness of  $\approx 2$  nm (Fig. 5c). The interplanar distance for the Re particles after fast Fourier transform filtering is  $d_{101} = 0.21$  nm. Rhenium clusters with a size of  $\approx 1$  nm are present in the zeolite channels (Fig. 5d).

The studies showed that, after the methane dehydroaromatization reaction, the 5.0% Re/ZSM-5 catalyst does not contain a rhenium carbide phase, whereas a molybdenum carbide phase is always present in Mo/ZSM-5 catalysts after exposure to methane. The absence of a rhenium carbide phase in a Re/ZSM-5 catalyst after reaction was also shown in [8]. Apparently, the absence of a rhenium carbide phase in the 5.0% Re/ZSM-5 catalyst is responsible for the low activity of this catalyst compared with the activity of the Mo/ZSM-5 sample.

Large molybdenum particles are observed on the zeolite surface in the 0.5%Re-4.0%Mo/ZSM-5 catalyst after 380 min on stream in methane conversion; the nature of these particles was studied in detail by HRTEM and electron paramagnetic resonance in [16] (Fig. 6a). The catalyst contains the highest amount of Mo-Re clusters with a size of less than 1 nm, which are localized in the channels and cavities of the zeolite (Fig. 6b). These clusters are aggregated to form larger particles (2–5 nm), which are localized in the large inner cavities and on the outer surface of the zeolite.



**Fig. 5.** High-angle annular dark-field STEM image of the 5.0% Re/ZSM-5 catalyst exposed to methane for 380 min: (a) Re particles, (b) carbon deposits on the zeolite surface, (c) a Re particle with carbon deposits, and (d) Re particles in the zeolite channels.

Unlike the catalyst containing 0.5% Re, the zeolite surface in the 1.0% Re–4.0% Mo/ZSM-5 sample, after reaction, contains, in addition to Mo particles, small and large elongated Re particles:  $I \times d = (20 - 30) \times (1-2)$  nm (Fig. 7a). In addition, Mo–Re clusters and nanoparticles localized in the channels and cavities of the zeolite are observed (Fig. 7b).

Thus, electron microscopic studies have shown that Re-Mo/ZSM-5 catalysts are characterized by the presence of a large number of Mo-Re clusters with a

size of <1 to 2–5 nm, which are localized both in the zeolite channels and on the outer surface. An increase in the Re concentration to 1.0% leads to the formation of small and large elongated Re particles. The formation of rhenium particles and Mo–Re clusters in the catalyst leads to an increase in the catalyst activity and stability in the nonoxidative conversion of methane [8]. The fact that the activity of the 5.0%Re/ZSM-5 catalyst is lower than the activity of the 4.0%Mo/ZSM-5 sample is attributed to the absence

PETROLEUM CHEMISTRY Vol. 59 No. 1 2019



Fig. 6. High-angle annular dark-field STEM image of the 0.5%Re-4.0%Mo/ZSM-5 catalyst exposed to methane for 380 min: (a) large Mo particles and (b) Mo-Re clusters.



Fig. 7. High-angle annular dark-field STEM image of the 1.0%Re-4.0%Mo/ZSM-5 catalyst exposed to methane for 340 min: (a) Re particles and (b) Mo–Re clusters.

of a rhenium carbide phase in it under methane dehydroaromatization reaction conditions.

Thus, rhenium modification of a Mo/ZSM-5 catalyst leads to an increase in the catalyst activity and stable on-stream time in methane conversion to aromatic compounds. The highest activity and stability is exhibited by the 0.5%Re-4.0%Mo/ZSM-5 catalyst. The increase in the catalyst activity is attributed to the

PETROLEUM CHEMISTRY Vol. 59 No. 1 2019

formation of Re particles and Mo–Re clusters that are active in this process.

## ACKNOWLEDGMENTS

This work was performed under the Basic Research Program of State Academies of Sciences, project no. V.46.2.1.

### REFERENCES

- 1. Y. Xu and L. Lin, Appl. Catal., A 188, 53 (1999).
- L. Wang, R. Ohnishi, and M. Ichikawa, J. Catal. 190, 276 (2000).
- A. Szoke and F. Solymosi, Appl. Catal., A 142, 361 (1996).
- R. Kojima, S. Kikuchi, H. T. Ma, et al., Catal. Lett. 110, 15 (2006).
- V. Abdelsayed, D. Shekhawat, and M. W. Smith, Fuel 139, 401 (2015).
- S. Maihi, P. Mohanty, H. Wang, and K. K. Pant, J. Energy Chem. 22, 543 (2013).
- V. I. Bukhtiyarov, V. I. Zaikovskii, A. S. Kashin, and V. P. Ananikov, Usp. Khim. 85, 1198 (2016).
- R. Ohnishi and M. Ichikawa, Catal. Surv. Jpn. 5, 103 (2002).

- 9. M. A. Ryashentseva and Kh. M. Minachev, Usp. Khim. **38**, 2050 (1969).
- 10. F. Solymosi, J. Cserenyi, A. Szoke, et al., J. Catal. 165, 150 (1997).
- D. Wang, J. H. Lunsford, and M. P. Rosynek, J. Catal. 169, 347 (1997).
- S. Liu, L. Wang, R. Ohnishi, and M. Ichikawa, J. Catal. 181, 175 (1999).
- 13. R. W. Borry, Y. H. Kim, A. Huffsmith, et al., J. Phys. Chem. B 103, 5787 (1999).
- 14. Y. Xu, Y. Shu, S. Liu, et al., Catal. Lett. 35, 233 (1995).
- 15. L. Wang, R. Ohnishi, and M. Ichikawa, J. Catal. **190**, 276 (2000).
- 16. V. I. Zaikovskii, A. V. Vosmerikov, V. F. Anufrienko, et al., Kinet. Catal. 47, 389 (2006).

Translated by M. Timoshinina