

UDC 541.128:542.97:542.941.7:547.21:549.67

DOI: 10.15372/CSD20180413

Exploration of the Promoting Effect of Nanoscale Copper Powder on Properties of Mo/ZSM-5 Catalyst in Methane Dehydroaromatization Reaction

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(Received July 13, 2018; revised July 28, 2018)

Abstract

The dry mechanical mixing of ZSM-5 catalyst with nanoscale powders (NSP) of molybdenum and copper produced Cu–Mo/ZSM catalysts. The Mo and Cu contents therein were 4.0 mass % and 0.05–1.0 mass %, respectively. In order to carry out comparison tests, Cu–Mo/ZSM-5 systems were prepared by impregnation of 4.0 % Mo/ZSM-5 catalyst with a $\text{Cu}(\text{NO}_3)_2$ solution and by its mechanical mixing with CuO. Acid characteristics of the resulting samples were investigated by ammonia temperature programmed desorption. The acid sites concentration and strength of catalysts were determined. It was found that the addition of 0.1 % copper nanopowder to 4.0 % Mo/ZSM-5 catalyst resulted in a reduced concentration of strong acid sites to 140 $\mu\text{mol/g}$. Whereas, a further increase in copper NSP concentration leads to their concentration growth to 153 $\mu\text{mol/g}$. Herewith, the activity of catalysts in methane conversion is reduced compared to 0.1 % Cu NSP sample. Methane conversion degree for 20 min of the reaction over Mo/ZSM-5 and 0.1%Cu–4.0 % Mo/ZSM-5 catalysts is 16.1 and 18.9 %, correspondingly. As demonstrated by research on methane conversion temperature in the presence of 0.1 % Cu–4.0 % Mo/ZSM-5 catalyst, an increase in temperature from 650 to 750 °C is accompanied by increasing methane conversion. For example, the latter is 7.9 and 18.9 % over the first 20 min of reaction at 650 and 750 °C, respectively. It was determined that the maximum methane conversion degree over 0.1 % Cu–4.0 % Mo/ZSM-5 catalyst was reached at 1000 h^{-1} space velocity of gas raw materials.

Keywords: ZSM-5 zeolite, molybdenum and copper nanopowders, acidity, activity, methane dehydroaromatization

INTRODUCTION

Currently, the issue of efficient utilization of gaseous hydrocarbons to produce valuable petrochemistry and organic synthesis products is immediate to meet environmental issues and protection. An efficient way to process natural and associated gas, the main component of which is CH_4 , is methane non-oxidative conversion to aromatic hydrocarbons in the presence of bifunctional zeolite catalysts. In order to increase the length of the steady operation of the most active Mo-containing catalysts, they are promoted with such metals, as

Y, Zr, Pt, and Fe [1]. As a general rule, Mo/ZSM-5 catalysts are produced by zeolite impregnation with an ammonium paramolybdate (heptamolybdate) solution [2–4] or solid-phase synthesis via zeolite mixing with molybdenum salt or molybdenum oxide followed by calcination [5, 6]. Promoting additives are introduced into the composition of Mo/ZSM-5 using similar methods too.

The present research paper gives the results of the investigations of non-oxidative methane dehydroaromatization (DHA) in the presence of Cu–Mo/ZSM-5 catalyst produced using nanoscale powders (NSP) of molybdenum and copper. Fur-

thermore, the effect of the procedure for copper introducing and concentrating in Mo/ZSM-5 catalyst and process conditions for methane conversion and the yields of its final transformation products was explored.

EXPERIMENTAL

High-silica zeolites (HSZ) with silica modulus (SM) of 40 were produced by hydrothermal synthesis using hexamethylenediamine as a structure-forming additive. Catalysts for methane dehydroaromatization process were prepared by the mechanical mixing of zeolite with nanoscale Mo-Cu powders. The latter were produced in the Institute of Strength Physics and Materials Science of Siberian Branch of the Russian Academy of Sciences (ISPMS SB RAS) by an electric explosion of corresponding conductors in argon medium [7]. The average particle size of molybdenum and copper was 70 nm. The metal copper content in the powder was about 98 mass %. The amount of active metal was reduced to 85–90 mass % in contact with air and mechanical mixing. Mixing samples was carried out in a KM-1 vibrating mill for 2 h, after which the resulting mixtures were calcined at 540 °C for 4 h. The Mo content in the catalyst was 4.0 mass %, whereas Cu concentration in the Cu-4.0 % Mo/ZSM-5 catalytic system was varied from 0.05 to 1.0 mass %. In order to carry out comparison tests, Cu-Mo/ZSM-5 systems were prepared by impregnation of 4.0 % Mo/ZSM-5 catalyst with a $\text{Cu}(\text{NO}_3)_2$ solution and by its mechanical mixing with CuO.

Acid properties of catalysts were investigated by temperature-programmed desorption (TPD) of ammonia. The method allows determination of the acid sites distribution according to strength, and also their concentration [8]. The latter in catalysts was determined according to the amount of ammonia desorbed at the moment of recording desorption peaks showing in micromoles per 1 g of catalyst.

Research on non-oxidative methane conversion (purity level of 99.99 vol. %) was performed in a flow setup at 650–750 °C, 500–1500 h^{-1} space velocity of gas raw materials, and air pressure. Reaction products were analyzed every 40 min of catalyst operation by GLC using a Chromatec-Crystal 5000.2 chromatograph. In order to assess the catalytic activity of samples, methane conversion degree and yields of resulting reaction products were determined.

RESULTS AND DISCUSSION

In order to evaluate a procedure to introduce copper into 4.0 % Mo/ZSM-5 catalyst, comparative tests of samples produced by mechanical stirring with nanoscale Cu powder and copper(II) oxide followed by impregnation with a $\text{Cu}(\text{NO}_3)_2$ solution were carried out. The copper content in all samples was 0.1 mass % per metal. Figure 1 gives research results on the effect of introducing copper into 4.0 % Mo/ZSM-5 catalyst on its activity in methane dehydroaromatization reaction. It can be seen that Cu-4.0 % Mo/ZSM-5 catalyst produced using copper NSP exhibits even higher activity and stability compared to samples obtained by impregnation and mechanical mixing with copper oxide. It is likely to be due to a more uniform distribution of Cu nanoparticles on the surface of zeolite catalyst during mechanical mixing.

Figure 2 gives research results on the effect of Cu NSP concentration on the activity and stability of 4.0 % Mo/ZSM-5 catalyst. This testifies that the formation of active sites resulting from methane reduction of molybdenum oxide (MoO_3) over these samples proceeds pretty quickly. There is a maximum activity of catalysts during the first 20 min of reaction.

The 4.0 % Mo/ZSM-5 catalyst containing 0.1 % of Cu nanopowder exhibits the maximum activity and stability in methane conversion. Methane conversion over 20 min of reaction over 4.0 % Mo/ZSM-5 and 0.1 % Cu-4.0 % Mo/ZSM-5 catalysts is 16.1 and 18.9 %, respectively. Increasing Cu NSP concentration in 4.0 % Mo/ZSM-5 catalyst to 0.5–1.0 % results in its activity and stabil-

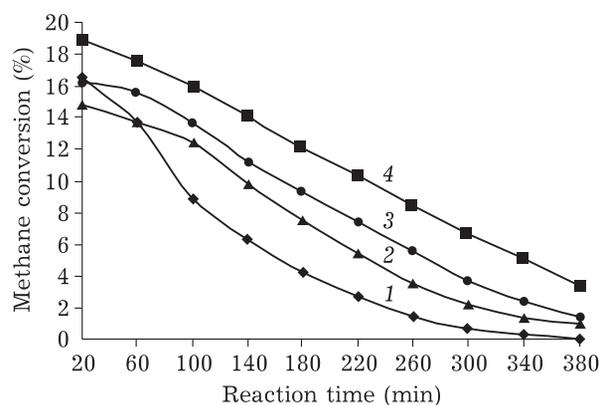


Fig. 1. Procedure for introducing Cu into 4.0 % Mo/ZSM-5 catalyst versus methane conversion: 1 - 0.1 % Cu (MM), 2 - 0.1 % Cu (I), 3 - 4.0 % Mo NSP, 4 - 0.1 % Cu NSP; MM indicates mechanical mixing with CuO, I - impregnation with $\text{Cu}(\text{NO}_3)_2$ solution, NSP - nanoscale powder ($T = 750$ °C, $W = 1000$ h^{-1}).

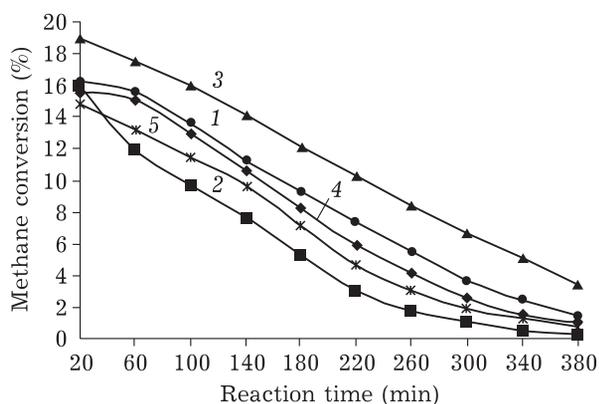


Fig. 2. Cu NSP concentration in 4.0 % Mo/ZSM-5 catalyst *versus* methane conversion ($T = 750\text{ }^{\circ}\text{C}$, $W = 1000\text{ h}^{-1}$), %: 0 (1), 0.05 (2), 0.1 (3), 0.5 (4), 1.0 (5).

ity decrease due to quick carbonization of the surface of the zeolite support.

As demonstrated by the analysis of methane transformation products over Cu-Mo-containing zeolite catalysts, they are mainly comprised of C_2 hydrocarbons (ethane and ethylene) and aromatic compounds (benzene, toluene, and naphthalene). Changing copper content in 4.0 % Mo/ZSM-5 catalyst has a slight effect on the composition of the generated gaseous products of methane transformation. The ethane yield in the course of reaction increases and reaches a maximum value of 0.12–0.13 % for 100–180 min. Ethylene content in products produced over copper-modified samples is higher than that over the initial Mo/ZSM-5, and there is the maximum ethylene yield (1.65 %) over 0.1% Cu–4.0% Mo/ZSM-5 sample. Ethylene concentration in reaction products is higher than the amount of ethane throughout the entire process.

The main liquid products of methane transformation on the catalysts under investigation are

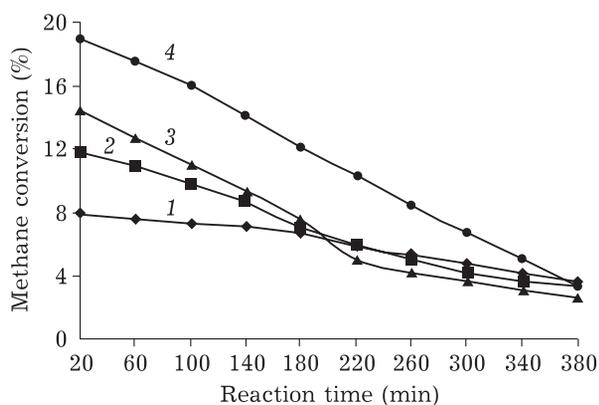


Fig. 3. Methane conversion *versus* 0.1 % Cu NSP–4.0 % Mo/ZSM-5 catalyst of operation time at process temperature ($^{\circ}\text{C}$): 650 (1), 700 (2), 720 (3), and 750 (4) ($W = 1000\text{ h}^{-1}$).

benzene and naphthalene. The yield of benzene in the beginning of the process does not depend on the concentration of Cu NSP in the catalyst and reaches 8.0–8.4 %. There is a reduction in the formation of benzene with increasing reaction time. This is most apparent for catalysts with high copper content. For example, the yield of benzene over 1.0 % Cu–4.0 % Mo/ZSM-5 sample is reduced from 8.4 to 0.16 % over the reaction time of 380 min.

Figures 3 and 4 give research results on the temperature effect and space velocity of methane on its conversion in the presence of 0.1 % Cu–4.0 % Mo/ZSM-5 catalyst. As can be seen from the data presented in Fig. 3, increasing reaction temperature from 650 to 750 $^{\circ}\text{C}$ is accompanied with methane conversion increase and this is most apparent at the beginning of the process. For example, methane transformation degree in the first 20 min of reaction at 650 and 750 $^{\circ}\text{C}$ is 7.9 and 18.9 %. There is the maximum degree of methane transformation during the entire time of testing 0.1 % Cu–4.0 % Mo/ZSM-5 catalyst at a 1000 h^{-1} space velocity (see Fig. 4).

Table 1 gives the results of investigating the effect of Cu NSP addition on acid characteristics of 4.0 % Mo/ZSM-5 catalyst. It can be seen, unmodified zeolite has two types of acid sites, which is indicated by the presence of two types of ammonia desorption in the thermodesorption spectrum that are weakly acidic and strongly acidic ones with maximum temperature (T_{max}) at 200 $^{\circ}\text{C}$ and $T_{\text{max}} = 420\text{ }^{\circ}\text{C}$, correspondingly. The concentration of weak and strong acid sites of ZSM-5 zeolite is 615 $\mu\text{mol/g}$ and 206 $\mu\text{mol/g}$, respectively. Introducing Mo into zeolite results in a decrease of both the concentration of acid sites and their strength, which is indicated by shifting the

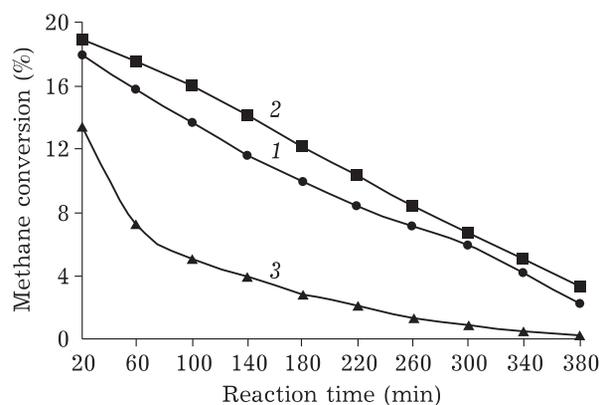


Fig. 4. Methane conversion *versus* 0.1 % Cu NSP–4.0 % Mo/ZSM-5 catalyst operation time at space velocity of initial raw materials (h^{-1}): 500 (1), 1000 (2), 1500 (3) ($T = 750\text{ }^{\circ}\text{C}$).

TABLE 1

Acid characteristics of catalysts

Catalyst	T_{\max} , °C			Concentration, $\mu\text{mol/g}$			
	T_{I}	T_{II}	T_{III}	C_{I}	C_{II}	C_{III}	C_{Σ}
ZSM-5	200	420	–	615	206	–	821
4.0 % Mo-ZSM-5	195	380	–	604	144	–	748
0.1 % Cu-4.0 % Mo/ZSM-5	180	380	–	581	140	–	721
0.5 % Cu-4.0 % Mo/ZSM-5	180	330	–	545	146	–	691
1.0 % Cu-4.0 % Mo/ZSM-5	175	325	510	515	153	48	716

Note. T_{I} , T_{II} , and T_{III} are temperatures of peak maxima for forms I, II, and III; C_{I} , C_{II} , C_{III} , and C_{Σ} are acid sites concentration in forms I, II, and III, and also total content, respectively.

maxima of both peaks to the low-temperature region.

There is the most significant decrease in the concentration and strength of acid sites for high-temperature ones that are usually referred to as Bronsted acid sites. The corresponding changes of acid characteristics of ZSM-5 zeolite are related to the interaction of Bronsted acid sites with molybdenum forms that take place during calcination in the process of catalyst preparation and is due to the formation of the $\text{Al}_2(\text{MoO}_4)_3$ phase.

The addition of copper nanopowder to 4.0 % Mo/ZSM-5 catalyst leads to even more reduction in the strength of acid sites. Herewith, a sharply defined peak with a maximum at 510 °C appears in the TD spectrum of the sample containing 1.0 % Cu NSP. This indicates the formation of new active sites driven by the presence of copper in the catalyst. When 0.1 % Cu NSP is added to 4.0 % Mo/ZSM-5 catalyst, the concentration of strong acid sites is reduced to 140 $\mu\text{mol/g}$, whereas increasing Cu NSP content to 0.5–1.0 % leads to a minor increase in the content of strong acid sites and even stronger ones (48 $\mu\text{mol/g}$) appear. Herewith, the catalysts demonstrate lower activities during methane conversion compared to the 0.1 % Cu NSP-containing sample.

CONCLUSION

During methane conversion into aromatic hydrocarbons, the addition of 0.1 % copper powder has a promoting effect on catalytic properties of

Mo-containing zeolite increasing its activity and stability. This is likely to be related to the uniform distribution of Cu nanoparticles on the surface of a zeolite carrier during mechanical mixing. These species migrate to zeolite channels and interact with Mo-containing active sites during calcination and in the course of the reaction. Due to this, zeolite lattice dealumination is suppressed, whereas the formation of new active sites slows down coke formation during methane dehydroaromatization.

Acknowledgements

The research work was carried out within the framework of Fundamental Research Programs of the State Academies of Sciences (project No. V.46.2.1).

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