Hydrogenation of Furfural to 2-Methylfuran over Ni-Mo_2C/γ-Al_2O_3 catalyst

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Abstract: - The current study focuses on the synthesis of a new supported catalyst by impregnation of the γ-Al_2O_3 solution of Ni and Mo salts and citric acid as carbon resource with the following temperature programmed treatment. Characterization of catalyst composition was performed using XANES/EXAFS method shown the presence of molybdenum carbide and metallic nickel. The oxide form of Mo and Ni were also detected. The supported catalyst was investigated in the hydrogenation reaction of furfural. The free-solution furfural conversion was carried out at a temperature of 160-260 °C and a hydrogen pressure of 5.0 MPa in a fixed bed reactor. The main hydrogenation products were furfuryl alcohol and 2-methylfuran. It was shown that 2-methylfuran formation increases with the reaction temperature and reaches around 75-80 %. High temperature leads to fast catalyst deactivation due to polymer formation on its surface.

Key-Words: - biomass, furfural, 2-methylfuran, fuel additive, hydrogenation, carbide catalyst

1 Introduction

Processing of renewable raw materials takes an important place among other alternative energy sources. In particular, furfural is a promising platform compound derived from lignocellulosic biomass, since it can be successfully converted to biofuels and chemicals [1-3]. Also, furfural can be processed to 2-methylfuran (2-MF), which is known as high-octane additive [4] with high blending research octane number of 131 and low boiling point of 64 °C, which is necessary for a cold-start exhaust emission test. In practice, 2-MF has already been studied as a component of a mixture with EN228 gasoline [5] has proved the high efficiency. Therefore, 2-MF is a very useful chemical compound for fuel upgrading and furfural is a feedstock for 2-MF production.

Usually, the industrial process of 2-MF production is carried out by furfural hydrogenation over Cu Cr catalytic systems. For example, it is well known that nearly 99 % yield of 2-MF can be achieved using supported Cu–Cr catalyst in the gas phase furfural hydrogenation [6]. Rarely, Pt or Pd based catalysts are used, but in this case, 2-MF is a by-product of furfural conversion into other value-added chemicals such as furan or tetrahydrofurfuryl alcohol [7]. Therefore, the main disadvantage of Pt or Pd based catalysts is the high cost of noble metals, as well as their low selectivity for 2-MF. Cu-Cr catalysts have a low price but they are prone to rapid deactivation, especially during the process of furfural hydrogenation in gaseous phase [8, 9]. Also, Cu-Cr catalysts have a detrimental effect on the environment, due to the high toxicity of Cr^{6+}.

Therefore, recently Mo carbide catalysts were suggested for hydrogenation of furfural. Xiong and colleagues investigated the furfural hydrogenation process by HREELS method and theory of functional density [10, 11]. They showed that molybdenum carbide strongly interacts with the aldehyde group of furfural, which corresponds to high selectivity of 2-MF formation. Lee et al. studied molybdenum carbide during gas phase hydrogenation of furfural, as a result, 60% selectivity for 2-MF was observed at temperatures of 150 °C. In our previous study, it was found that high-loading molybdenum carbide-based catalyst has very low activity [12]. To increase the activity we suggested using Ni addition to molybdenum carbide systems. Catalysts with Ni/Mo atomic ratio less than 1 were reported to be significantly more reactive than conventional molybdenum carbide and they have 100 % selectivity pathway of 2-MF formation from furfuryl alcohol. However, it was shown that such Ni-Mo carbide systems have a low total surface area of about 11 m^2/g. In addition, these catalysts have bad formability and they could not be used in a fixed-bed reactor. So the following study and improvement are needed. Preparation of supported Ni-Mo carbide catalysts could solve the above disadvantages.

In the current research, we propose the study of alumina supported Ni-Mo carbide catalysts in the process of liquid phase furfural hydrogenation to 2-methylfuran. The catalyst was prepared, characterized by XANES/EXAFS method and tested in furfural hydrogenation in a fixed-bed reactor.

2 Experimental

2.1 Preparation of Ni-Mo_2C/γ-Al_2O_3 catalyst

Carbide catalyst Ni-Mo_2C/γ-Al_2O_3 with molar ratio Ni/Mo = 0.1 was prepared by the modified Pechini-based method using citric acid (99%, Reachim) as a polymerization/complexation agent. To obtain ratios of metals equal to 0.1 appropriate amounts of $Ni(NO_3)_2 \cdot 6H_2O$ (98%, Reachim) and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (98%, Reachim) were dissolved in water under stirring. Then citric acid (CA) was added. After the formation of a homogeneous solution, it was used for impregnation of γ-Al_2O_3 (Sasol, Germany) for supported catalyst formation. The sample was then dried at 110 °C for 10 h followed by calcination in a quartz reactor at 400 °C under an inert atmosphere for 5 h. To prevent oxidation of the synthesized carbide upon exposure to air, the catalyst was cooled down and passivated for 5 h in 1% O_2/Ar at room temperature. Then the passivated sample was reduced at 600 °C under hydrogen flow. After hydrogen treatment, the catalyst was cooled down and passivated.

The carbide catalyst with high-metal loading Mo_2C-SiO_2 was prepared by the same method with the difference that nickel nitrate was not used and ethylsilicate-32 was added to the homogeneous solution to stabilize the active component instead of the impregnation stage.

2.2 Catalytic Activity and Selectivity Tests

The selective hydrogenation was studied in a tubular fixed bed flow reactor. The reactor was made of stainless steel (inner diameter 14 mm, length 300 mm). It was heated with an electric furnace and the temperature was monitored with a thermocouple in the reactor. The experiments were carried out at P=5.0 MPa and T=160–260 °C. The feed rate of hydrogen was 18 L/h. Solvent-free furfural was used as the substrate. The substrate feed rate, U, was 3 ml/h, the contact time, τ, was 1 h, and the catalyst volume, Vcat, was 3 cm^3. Before the experiments, the catalysts (fraction 0.25/0.5 mm) were in situ reduced at 300 °C in a hydrogen flow at 0.1 MPa for 1h. Then the reactor was cooled to the desired temperature, the hydrogen pressure was raised to 5.0 MPa and the substrate was added to the feed. The liquid phase was sampled at least once an hour.
Qualitative analysis of liquid products of the hydrodeoxygenation of furfural was carried out using a Varian Saturn 2000 GC/MS spectrometer equipped with an ion trap and a WAX capillary column. Quantitative analysis of the liquid products was performed using an Agilent Technologies GC-7820A chromatograph equipped with a Zebron ZB-5HT and WAX capillary columns.

2.3 Catalyst Characterization

The phase composition of the samples calcined at 400 °C in an inert atmosphere, and reduced and passivated catalysts was studied using a D8 X-ray diffractometer (Bruker, Germany) equipped with a Lynxeye linear detector. The XRD patterns were obtained in the 2θ range from 15° to 80° with a step of 0.05° using monochromatic Cu Kα radiation (λ = 1.5418 Å).

The XANES/EXAFS study was performed at the Structural Materials Science beamline at the Kurchatov Synchrotron Radiation Source (National Research Center “Kurchatov Institute”, Moscow, Russia). The experimental station was described in detail in [13]. The spectra were obtained at the Mo K-edge and Ni K-edge in the transmission mode using a channel-cut Si(220) and Si(111) monochromators, respectively. To measure the X-ray absorption, the powder of the samples under study was placed between thin Kapton films. Simultaneously with the spectrum of each catalyst, the absorption spectra of metallic molybdenum or nickel were recorded for calibration. The ionization currents were measured by Keithley 6487 digital picoamperemeters (Keithley Instruments LLC, USA).

3 Results and discussion

Figure 1 shows the XRD patterns of the studied carbide catalysts. For a catalyst with a high metal content Ni-Mo2C-SiO2, the broad peaks of the cubic structure of molybdenum carbide fcc-Mo_2C are observed. The average size (coherent scattering domains - CSD) was calculated using 111 reflections and was about 30 Å. In addition, the shoulder about 43.8° and the background at 51.5° can correspond to metallic nickel, however, it was not possible to determine the average particle size for this form of peaks. For a supported catalyst, only reflections of γ-Al_2O_3 are present in the diffraction pattern. The metallic or carbide phases were not observed. Probably, the active component is in an amorphous state or its quantity is not enough for identification.

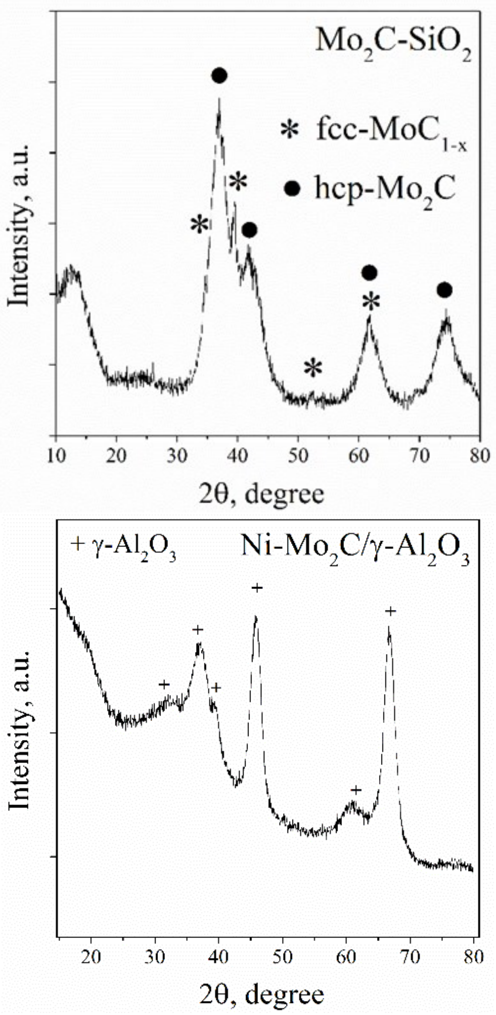

Fig.1. XRD patterns of the Mo_2C-SiO_2 and Ni-Mo_2C/γ-Al_2O_3 catalysts

Molybdenum carbide supported on alumina has already been studied in a number of papers devoted to catalytic processing of various raw materials. Also, alumina supported molybdenum carbide was characterized using various physicochemical methods. Wu et al. [14] studied the structure and phase content of hexagonal hcp-Mo_2C/Al_2O_3 using X-ray diffraction analysis and X-ray photoelectron spectroscopy. As a result, carbide particles were shown to be highly dispersed, therefore XRD patterns of hcp-Mo_2C/Al_2O_3 have only peaks from Al_2O_3. In addition, the article studied the adsorption of CO on the catalyst surface by FT-IR spectroscopy. According to data obtained, hcp-Mo_2C/Al_2O_3 catalyst demonstrates properties of noble metals in CO adsorption.

A series of Mo and Ni K- edges XANES spectra of the Ni-Mo_2C/γ-Al_2O_3 and Mo_2C-SiO_2 sample, and standard compounds (Ni, NiO, Mo, MoO_2, MoO_3) are presented in Figure 2.

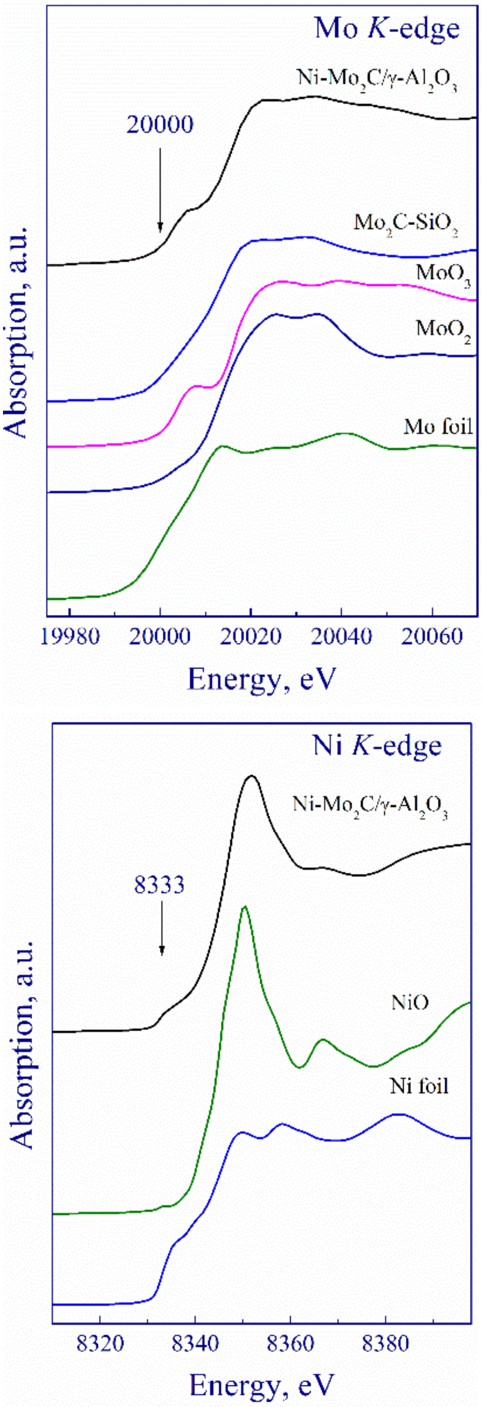

Fig.2. The XANES spectra of Mo K-edge for standards (Mo, MoO_2, MoO_3), nigh-metal loading Mo_2C SiO_2 and supported Ni-Mo_2C/γ-Al_2O_3 catalysts; Ni K-edge for standards (Ni, NiO) and supported Ni-Mo_2C/γ-Al_2O_3 catalyst.

The absorption value for K-edge was determined from the maximum of the first derivative of the

XANES spectra; for metallic molybdenum, the absorption energy for Mo K-edge is 20,000 eV [15]. The Mo K-edge XANES spectra in the Ni-Mo_2C/γ-Al_2O_3 sample under study have a similar shape and are similar to the spectrum of Mo_2C–SiO_2, which was used as a standard for molybdenum carbide. This suggests that molybdenum carbide is present in the supported samples. The pre-edge in the spectra of the sample under study is shifted relative to the pre-edge of metallic molybdenum by about 6 eV towards higher energies, which may be due to the transfer of a negative charge from molybdenum in Mo_2C to the support γ-Al_2O_3 [16-17]. The XANES spectra of the sample under study have pre-edge features that appear during electronic transitions to bound excited states. As is known, the intensity of the pre-edge peaks is sensitive to the symmetry of the chemical environment of the absorbing atom. On the spectrum of the Ni-Mo_2C/γ-Al_2O_3 sample, a small shoulder is observed at the K-edge in the region of 20007 eV. Such a feature in the XANES spectra is observed when electronic transition 1s to hybridized 4d and 5p molecular molybdenum orbitals mixed with 2p oxygen orbitals become possible. Mixing occurs due to the centrosymmetric chemical environment of molybdenum atoms with oxygen atoms [18]. A similar shoulder at the K-edge is observed in the MoO_3 spectrum, while in the MoO_2 spectrum, such a shoulder is not observed. From the XANES analysis of the Mo K-edge, it can be argued that molybdenum is present in the Ni-Mo_2C/γ-Al_2O_3 sample in the oxidation state of +6 and some atoms are in the structure of molybdenum oxide MoO_3. Wu et al. [14] showed that the sample hcp-Mo_2C/Al_2O_3 obtained by carburizing MoO_3/Al_2O_3 contains molybdenum in the form of carbide, oxycarbide and oxide, which indicates the incomplete reduction of MoO_3 and important role of passivation stage in catalyst formation.

The K-edge of metallic nickel is at 8333 eV [15]. The XANES spectrum of metallic nickel is characterized by the presence of two well-defined absorption bands in the region of 8350-8360 eV of approximately with the same intensity and by the shoulder in the region of 8335 eV (transition 1s → 3d). In contrast to the XANES spectrum of metallic nickel, the NiO spectrum has an intense peak at the absorption bands at 8350 eV [18-19]. The Ni K-edge XANES spectra of the catalyst under study have a clear peak in the region of 8351.0 eV characterizing the nickel in the oxide form. The pre-edge feature presented by the shoulder at 8335 eV is characteristic of the XANES spectrum of nickel foil. It can be assumed that the sample contains a mixture of two nickel phases in a metallic and oxidized state.

The results of simulating of the XANES spectra into a linear combination of the spectra of standard compounds (Mo, MoO_2, MoO_3, and Ni, NiO) and Mo_2C-SiO_2 as molybdenum carbide standard are presented in Fig. 3. As a result of the decomposition of the Mo K-edge of the Ni-Mo_2C/γ-Al_2O_3 sample under investigation into a linear combination of the spectra of standards, it was found that molybdenum is contained in MoO_3 and Mo_2C-SiO_2 in a ratio of approximately 58:42. The metallic component of molybdenum in Ni-Mo_2C/γ-Al_2O_3 was not detected. An analysis of the Ni K-edge shows that about 68% of nickel atoms in the Ni-Mo_2C/γ-Al_2O_3 sample are in the composition of NiO and about 32% are in the metallic state, while the possible presence of a carbide nickel was not taken into account.

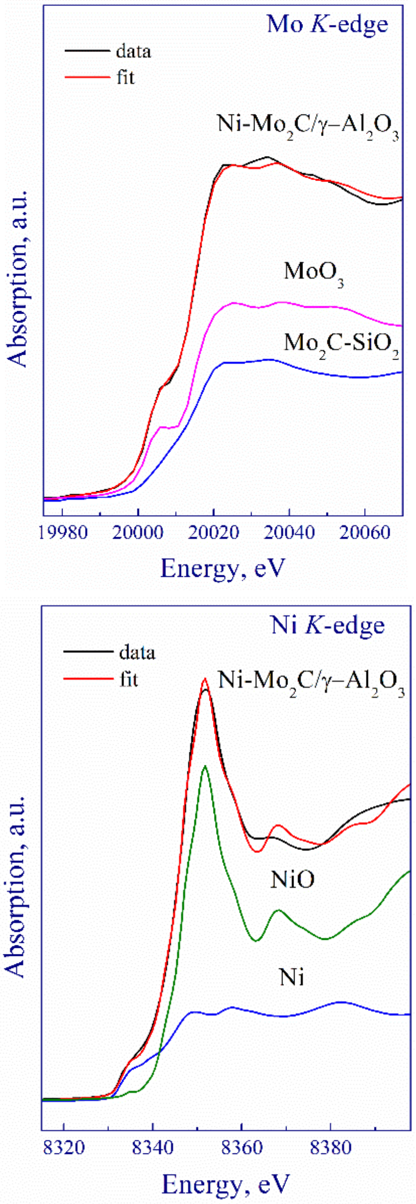

Fig.3. Simulating of the Mo K-edge XANES spectra and Ni K-edge XANES spectra of Ni-Mo_2C/γ-Al_2O_3 catalyst.

Thus, in a sample of Ni-Mo_2C/γ-Al_2O_3, molybdenum and nickel oxides, molybdenum carbide and nickel in a metallic state are present in large quantities.

The Fourier transform of the $k^2\chi(R)$ EXAFS oscillations observed at the Mo and Ni K-edge of in the studied sample is shown in Fig. 4.

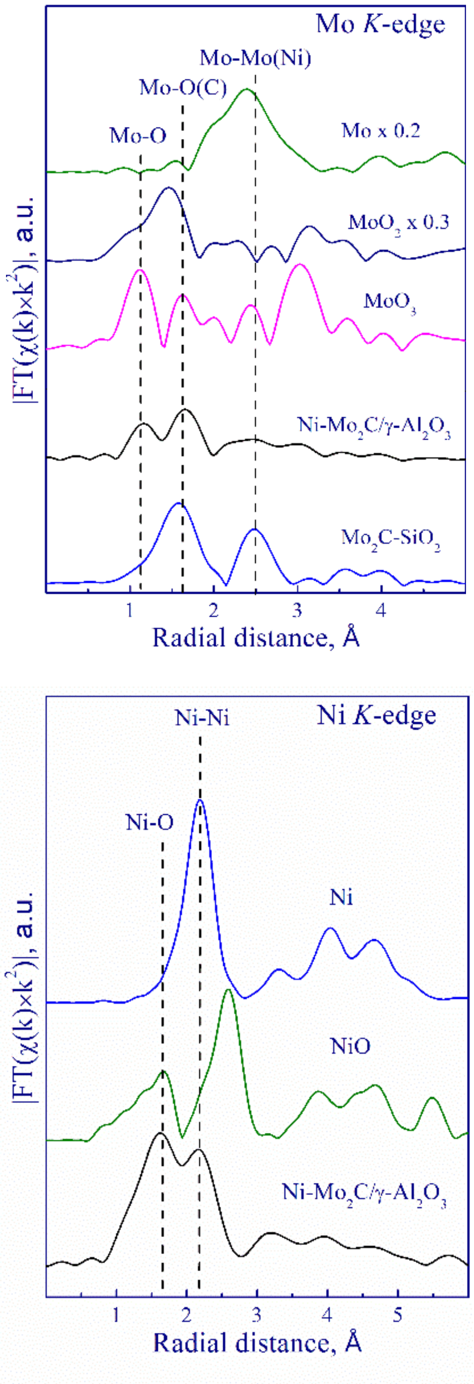

Fig.4. Radial distribution function of atoms around molybdenum obtained from Mo K-edge and nickel obtained from Ni K-edge EXAFS spectrum for the supported Ni-Mo_2C/γ-Al_2O_3 catalyst.

The EXAFS curve show peaks near 1.1 Å of the molybdenum K-edge, which is also present on the EXAFS-curve of molybdenum oxide (MoO_3) and corresponds to the Mo-O distances. That molybdenum oxide is present in the composition of Ni-Mo_2C/γ-Al_2O_3 with respect to the analysis of XANES spectra. However, an intense peak of 3.1 Å characterizing of molybdenum oxide in the samples, is absent. This indicates that there is no local ordering beyond 3 Å in the studied sample, that why, molybdenum oxide is probably in the amorphous state, either in the form of a thin film or in a strongly dispersed state. The peak at 2.5 Å corresponding to the bond distance of Mo-Mo is low-intensity, and therefore molybdenum carbide in the supported catalyst is in a highly disordered form. At the Ni K-edge in the Ni-Mo_2C/γ-Al_2O_3 sample, two peaks are observed in the region of 1.6 and 2.2 Å, which corresponds to the Ni-O distance in nickel oxide and Ni-Ni in metallic nickel, which confirms the presence of nickel in the oxide and metal form. However, there is an intense peak at 2.6 Å in nickel oxide, which corresponds to the Ni-Ni distance, which is not observed on the EXAFS curve. We can conclude that the local order in the oxide component of nickel-containing samples is formed only within ~ 2 Å and nickel oxide, like molybdenum oxide, in the studied sample is in the amorphous state, either in the form of a thin film or in a strongly dispersed state.

Thus, based on the analysis of XANES spectra, we can conclude that the proposed method for the synthesis of supported carbide catalysts allows obtaining Ni-Mo_2C/γ-Al_2O_3 sample, in which there are particles of metallic Ni (it is the possible formation of Ni-Mo alloy based on nickel with a low content of Mo). Most of the nickel and molybdenum is found in nickel oxide, molybdenum oxide and carbide forms. The metal oxides included in the composition of the samples are in a strongly amorphous state, which prevents their detection by XRD.

Studies on the optimization of the process temperature were carried out in a flow reactor. The hydrogen rate (18 L/h) and high hydrogen pressure (5 MPa) remained constant in all experiments. For the study, the catalyst Ni-Mo_2C/γ-Al_2O_3 was investigated in the process of hydrogenation of furfural at temperatures of 160, 200 and 260 °C. Liquid samples were taken every hour to determine the conversion of furfural and the yields of the main reaction products. In the analysis, the sample taken at 1 hour was not taken into account, since its quantity was very small. In the reaction of hydrogenation of furfural (FUR), the formation of furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), 2-methylfuran (2-MF), 2-methyltetrahydrofuran (2-MTHF), and difurfuryl ether (DFE) was observed. Based on the analysis of liquid products of furfural hydrogenation, a reaction scheme has been proposed (Fig. 5)

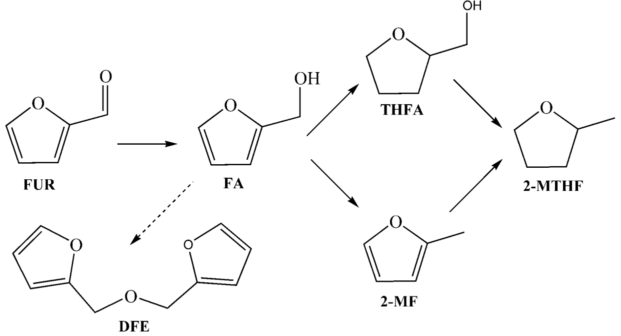

Fig.5. Scheme of furfural conversion on supported carbide catalysts (The reaction was carried out at T = 160-260 °C, P = 5 MPa of H_2, V_{FUR} = 3 mL/ч, V_{H_2} = 18 L/h V_{cat} = 3 mL).

As a result of research, it was found that with an increase in temperature, the activity of the catalyst in hydrogenation increases, which leads to an increase in the yield of 2-methyltetrahydrofuran to 60 mol.% at a temperature of 260 °C (Fig. 6). In the entire temperature range of 160–260 ° C, high furfural conversions (100%) are observed. At lower temperatures, hydrogenation of furfural mainly occurs with the formation of furfuryl alcohol with the partial formation of 2-methylfuran. At a temperature of 200 and 260 ° C, the best yields of 2-methylfuran are observed, the amount of which reaches 75 and 87 mol.%, respectively. However, the high temperature leads to fast deactivation of the catalyst with a decrease of yield of 2-MF. In addition, the gas phase of the reaction was studied, which included hydrogen as the main component, while the molar content of the C1-C3 gaseous products did not exceed 1 mol.% of the gas phase, which indicates that furfural and its hydrogenation products do not decompose on the surface catalyst with the formation of gaseous products but the accumulation of poly-furfuryl products occurred. The polymer formation can be caused be the acidity of γ-Al_2O_3 since on high-loading catalysts stabilized be SiO_2 the carbon deposits were not observed.

The catalyst after the reaction was studied by CHNS analyzer to define the carbon content. It was shown that the carbon quantity increased by 23, 40, 64 % for 160, 200 and 260 °C compared to the fresh sample. The high content of carbon is due to the fast formation of furfuryl-based polymers on catalyst surface leading to its deactivation.

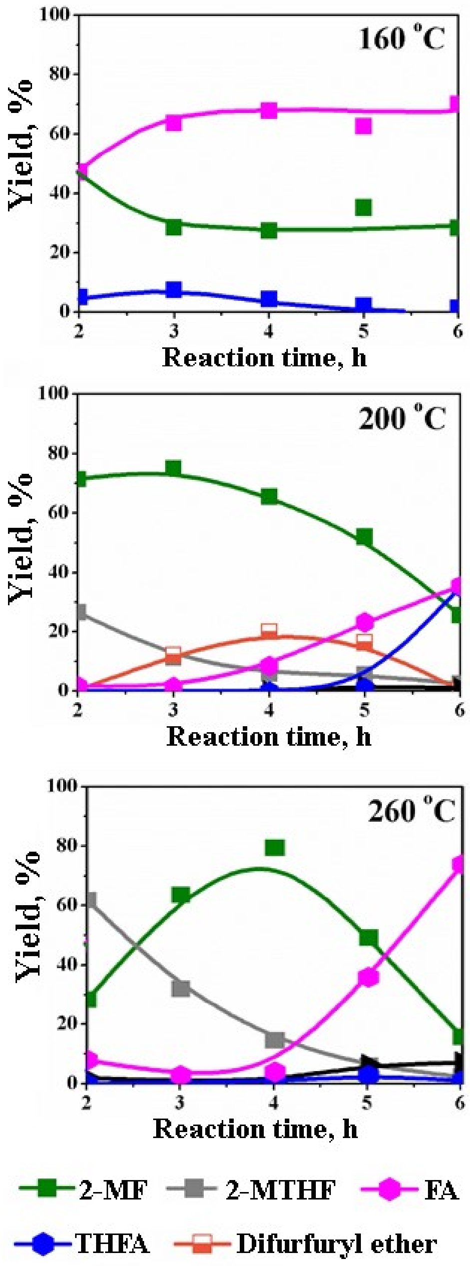

Fig.6. Yield of products in furfural hydrogenation (The reaction was carried out at T = 160-260 °C, P = 5 MPa of H_2, V_{FUR} = 3 mL/ч, V_{H_2} = 18 L/h V_{cat} = 3 mL).

According to previously research, the high selectivity of 2-MF formation can be due to the bifunctional nature of Ni-Mo_2C/γ-Al_2O_3 catalyst. Molybdenum carbide leads to selective furfural adsorption on the surface and metallic nickel contributes hydrogen activation for furfural hydrogenation.

4 Conclusion

The new supported molybdenum carbide catalyst modified by nickel was prepared and studied in the hydrogenation of free-solvent furfural in fixed bed reactor. According to XANES/XAFS method the formation of carbide molybdenum and metallic nickel leading high selectivity of 2-methylfuran formation was confirmed. A scheme for the reaction contains pathway of formation of furfural alcohol and difurfuryl ether as a by-product. Further hydrogenation of furfuryl alcohol separates into two pathway with tetrahydrofurfuryl alcohol, 2-methylfuran and 2-methyltetrahydrofuran formation. The study of catalyst activity in a fixed bed reactor in different temperature conditions showed that the maximum yield of 2-MF is 80% at 200-260 ° C, but then this value decreases, which is apparently due to the formation of carbon deposits on its surface. CHNS analysis showed that the content of carbon residues in the catalysts after 6 hours of reaction increases from 23 to 64 wt.% with an increase in the reaction temperature from 160 to 260 degrees.

The further study can focus on the increase of catalyst stability with selection of additives based on transition metals including Cu, Fe etc.

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