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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

# Hydro-Oxygenation of Furfural in the Presence of Ruthenium Catalysts Based on Al-HMS Mesoporous Support

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**Abstract**—Ruthenium-containing catalyst based on an Al-HMS mesoporous aluminosilicate was synthesized, The mesoporous support and the catalyst on its basis were characterized by the methods of low-temperature desorption/adsorption of nitrogen, temperature-programmed desorption of ammonia, transmission electron microscopy, X-ray photoelectron microscopy, and energy-dispersive X-ray fluorescence analysis. The catalyst obtained was examined in the reaction of hydrodeoxygenation of the model compound of bio-oil, furfural, in the presence of water. The reaction was performed at initial hydrogen pressures of 1–7 MPa in the temperature range 200–300°C. It was shown that the catalyst under study exhibits a high activity in the hydrotransformation of furfural: the conversion was 100% in 1 h at a hydrogen pressure of 5 MPa and temperature of 200°C.

Keywords: hydrodeoxygenation, furfural, mesoporous material, nanoparticles, ruthenium

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An increased interest is presently observed in the processing of renewable phytogenic raw materials for obtaining biofuel and valuable chemical products. One of promising sources of biofuel is the lignin-cellulose biomass formed as wood wastes of nonfood industries [1]. The technology of fast pyrolysis makes it possible from this biomass the product named bio-oil [2]. Bio-oil contains hundreds of organic products formed in thermal decomposition of the polymers in the biomass: cellulose (30-40 wt %, hemicellulose (20-30 wt %, and lignin (20-25 wt %), which belong to different classes: lowmolecular alcohols, acids, esters, aldehydes, ketones, furans, and also phenols of varied structure [1]. The main compounds formed in the pyrolysis of cellulose are levoglucosan, hydroxyacetaldehyde, hydroxyacetone, furfural, and 5-hydroxymethylfurfural. Pyrolysis of hemicellulose yields acetic acid, glycol aldehyde, furfural, and anhydro sugars, and that of lignin gives guaiacols, phenols, and syringoles of varied structure [3]. The distribution of components in bio-oil directly depends on the type of a biomass and on the conditions of fast pyrolysis.

The complex chemical composition, high content of oxygen and water formed in the pyrolysis of the biomass provide a high polarity and acidity of bio-oil, its thermal instability and immiscibility with hydrocarbons. To improve the quality of bio-oil and enable its joint processing with hydrocarbon oil products on the conventional oil-processing equipment, an additional stage of bio-oil upgrading is necessary. The main methods for bio-oil upgrading are the esterification [4], catalytic cracking [5], and catalytic hydrodeoxygenation (HDO) [6]. A disadvantage of bio-oil upgrading is the insufficiently effective removal of oxygen from bio-oil, which may lead to its repolymerization [7]. The catalytic cracking is characterized by a fast deactivation of a catalyst, which results from its coking, and by the low yield of the liquid product, caused by the loss of carbon due to the reactions of decarbonylation/decarboxylation [8]. Furthermore, one or several stages of hydroprocessing are commonly performed prior to the cracking in order to stabilize and deoxygenate bio-oil [9]. Therefore, a promising technology for upgrading of bio raw materials is HDO, during which oxygen is removed from bio-oil in the form of water, and the coking level is substantially lower than that in the catalytic cracking [10].

Development of HDO catalysts exhibiting activity in the processing of such a specific bio raw material as biooil is a topical task of petrochemistry. There exist a wide variety of HDO catalysts: conventional NiMoS/Al<sub>2</sub>O<sub>3</sub> and CoMoS/Al<sub>2</sub>O<sub>3</sub> [11], catalysts based on transition (Ni [12], Cu [13], Mo [14], W [15], Fe [16]) or noble (Rh, Ru, Pt, Pd [17]) metals and mixtures of these [18–20]. Of interest are catalysts based on noble metals and, in particular, Ru-containing catalysts because in the case of their application there is no need to introduce sulfur compounds into the reaction system. These catalysts are active and stable in processes occurring in the presence of water formed in substantial amounts in the HDO reactions with bio-oil and can provide an effective hydrogenation/ deoxygenation even under mild process conditions [21]. The activity of HDO catalysts and the distribution of reaction products are strongly affected by the nature of a support. In the presence of water, the classical  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is transformed into boehmite AlO(OH), which blocks and deactivates the active centers of the catalyst [22]. As alternative to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can serve the following: zeolites [23]; oxides ZrO<sub>2</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, CeO<sub>2</sub>, and mixtures of these [19, 24]; and carbon supports [25]. A disadvantage of the latter is their difficult regeneration under industrial conditions [1]. Of particular interest is the HDO with mesoporous supports. It has been noted in studies concerned with the HDO of model compounds of biooil in the presence of catalysts based on oxides Al<sub>2</sub>O<sub>3</sub>,  $ZrO_2$ ,  $TiO_2$ ,  $SiO_2$  and their mesoporous analogs that these latter exhibit a higher catalytic activity, manifested in the larger degrees of deoxygenation and conversion of the substrate [26-30].

Furfural is frequently used as a model compound in studies of the bio-oil HDO mechanisms because of being one of the main products formed in the pyrolysis of the cellulose/hemicellulose part of the biomass and containing the furan and carbonyl groups characteristic of the bio-oil composition. The goal of our study was to examine the activity of the Ru-containing catalysts synthesized in the study on the basis of the Al-HMS mesoporous material in the reaction of hydroxydeoxygenation of the model compound of biooil, furfural, in the presence of water.

### EXPERIMENTAL

Synthesis of Al-HMS mesoporous material. The Al-HMS mesoporous material (Si/Al = 10) was synthesized by the procedure similar to that reported in [30]. As reagents served hexadecylamine ( $C_{16}H_{35}N$ , Sigma-Aldrich, 98%), aluminum sec-butoxide (Sigma-Aldrich, 97%), tetraethoxysilane (Sigma-Aldrich, 99.99%), isopropanol (IPA, IREA 200, analytically pure), and distilled water. The gel containing the Al-HMS template had the following molar composition:  $20SiO_2 : Al_2O_3 :$  $5C1_6H_{35}N : 166IPA : 888H_2O.$ 

Synthesis of the Ru/Al-HMS catalyst. The typical procedure for synthesis of the Ru/Al-HMS catalyst includes impregnation of the support material with a solution of a ruthenium salt in methanol (Sigma-Aldrich, 99.8%), followed by removal of the excess of the solvent on a rotor evaporator. For this purpose a calculated amount of the support was added at 25°C to a solution of the metal salt in 30 mL of methanol. The mixture was agitated for 12 h. Then, a sample was dried in an air flow at 60°C for 6 h and then at 100 and 250°C for 3 h at each temperature. The resulting sample was suspended in 15 mL of methanol and 15 mL of water. Then 15 mL of a cooled aqueous solution of NaBH<sub>4</sub> (Sigma-Aldrich,  $\geq$ 98.0%) was added portionwise to the suspension (NaBH4/Ru molar ratio 10). The reduction was performed in the course of 12 H. To remove sodium borate formed as a by-product, the resulting mixture was three times washed with water and then three times with methanol. The catalyst produced after the reduction was dried in air and then at 60, 100, and 250°C for 3 h at each temperature. Ruthenium(III) chloride (Aurat, mass fraction of ruthenium  $\geq 46.5\%$ ). When the metal salt solution was prepared, the amount of RuCl<sub>3</sub> was calculated so that the theoretical content of ruthenium in the catalyst was 2 wt % (according to the results of an energy-dispersive X-ray fluorescence analysis the content of Ru was 1.79 wt %).

Instruments and methods. The nitrogen adsorption/ desorption isotherms were recorded at a temperature of 77 K on a Gemini VII 2390 instrument. Prior to measurements, the samples were degassed at 350°C for 6 h. The specific surface area was determined by the BET method with the use of adsorption data at relative pressures (p/p0) in the range 0.04–0.20. The pore volume and the pore size distribution were determined from the adsorption branch of the isotherms by using the Barrett–Joyner–Halenda model. The specific pore volume was determined from the amount of nitrogen adsorbed at a relative pressure  $p/p_0 = 0.99$ .

The acidity of a catalyst sample was determined by the method of temperature programmed desorption of ammonia (TPD–NH<sub>3</sub>) on a Micromeritics Auto Chem HP Chemisorption Analyzer instrument. A sample under study was crushed; the 1–2-mm fraction was selected, placed in a reactor and kept in a flow of helium at 400°C for 30 min. Then, the temperature was lowered to 100°C and the sample was saturated with ammonia for 30 min.

The physically adsorbed ammonia was blown away in a flow of helium until the zero line ceased to drifty. Then the reactor temperature was raised to 750°C at a rate of 20 deg min<sup>-1</sup>. The amount of ammonia desorbed in the course of the TPD was calculated with Auto Chem HP V2.04 software.

The catalyst was examined by transmission electron microscopy (TEM) on a Jeol JEM-2100 microscope at magnifications of 50 to 1 500 000 at image resolution of 0.19 nm at 200 kV.

The content of ruthenium was determined by energydispersive X-ray fluorescence analysis (EDXFA) on a Thermo Fisher Scientific ARL Quant'X analyzer in a vacuum. The results obtained were processed by using the no-standard UniQuant method. Samples were prepared as follows: powdered samples were compacted into pellets on a boric-acid substrate and covered with a Lavsan film pressed with an annular holder to a cuvette.

Measurements by the method of X-ray photoelectron spectroscopy (XPS) were made on a Kratos Axis Ultra DLD instrument. Photoelectrons were excited by the X-rays from the aluminum anode (Al $K_{\alpha}$  = 1486.6 eV. The photoelectron peaks were calibrated against the carbon line C1s with binding energy of 284.4 eV. The pass energy of the energy analyzer was 160 eV (survey spectrum) and 40 eV (separate lines).

Catalytic experiments. The catalytic experiments on HDO of furfural were performed at an increased hydrogen pressure an vigorous agitation in a 45-mL steel autoclave equipped with a magnetic rabble and glass insert-tube in which a calculated amount of the catalyst (0.1 g) and a model mixture containing 0.25 g of furfural (Sigma-Aldrich, 99%) and 1 g of water were placed. The autoclave was hermetically sealed and filled with hydrogen to a pressure of 1-7 MPa. The reaction was performed in the temperature range 200-300°C in the course of 0.5-4 h, with the temperature monitored with a thermocouple. After the reaction was complete, the autoclave was cooled to below room temperature. The catalyst was separated from the solution by centrifugation. To provide a full dissolution of organic compounds and homogenization of the reaction mixture, isopropanol was added to a sample before a chromatographic analysis. The hydrogenation products were analyzed on a Kristallyuks 4000 M chromatograph equipped with a PID and a Petrocol® DH 50.2 column with polydimethylsiloxane as fixed liquid phase (50 m  $\times$  0.25 mm, carrier-gas helium, flow division 1 : 90). Additionally, liquid products were analyzed by chromato-mass spectrometry on Finnigan MAT 95 XL instrument equipped with a chromatograph with Varian VF-5MS capillary column (30 m × 0.25 mm × 0.25 mm), carrier-gas helium (1.5 cm<sup>3</sup> min<sup>-1</sup>).

## **RESULTS AND DISCUSSION**

The procedure used to synthesize the Al-HMS support and its characteristics were described in more detail earlier in [30]. The main physicochemical characteristics of the Al-HMS mesoporous support are

Support	Surface area according to the BET model, m <sup>2</sup> g <sup>-1</sup>	Pore diameter, Å	Pore volume, cm <sup>3</sup> g <sup>-1</sup>	Total number of acid centers, μmol g <sup>-1</sup> NH <sub>3</sub>
Al-HMS <sup>a</sup>	935	35	1.04	286

<sup>a</sup> SiAl molar ratio in the Al-HMS sample is 10.

presented below:

The Al-HMS sample has a high specific surface area of 935  $m^2 g^{-1}$  and mesoporous structure, which is confirmed by the low-temperature nitrogen adsorption/desorption

data according to which the sample is characterized by a type-IV isotherm with a hysteresis loop. According to TPD-NH<sub>3</sub>, the total number of acid centers in the Al-HMS support (Si/Al = 10) is 286  $\mu$ mol g<sup>-1</sup> NH<sub>3</sub>. The material



Fig. 1. (a) TEM micrograph of Ru/Al-HMS and (b) ruthenium particle size distribution.

mostly contains medium-strength acid centers ( $T_{\text{max}} \approx 300-500^{\circ}\text{C}$ ) and a minor amount of strong acid centers ( $T_{\text{max}} > 500^{\circ}\text{C}$ ) [29].

After the metal was deposited, the Ru/Al-HMS catalyst was characterized by the methods of TEM and XPS. According to TEM, Ru/Al-HMS has an ordered structure with ruthenium particles uniformly distributed over the surface of the support. Distinct channels and hexagonally ordered mesopores with sizes of 30–40 Å can be distinguished in TEM micrographs (Fig. 1a). The average size of ruthenium particles is 1.4–1.8 nm (Fig. 1b).

Figure 2 shows a high-resolution part Ru3*d* of the XPS spectrum for a Ru/Al-HMS sample. Because of the superposition of lines C1*s* (285 eV) Ru3*d*<sub>3/2</sub> only the component Ru3*d*<sub>5/2</sub> (280.1 eV) can be reliably identified. However, the deconvolution of the spectrum demonstrated the presence of two ruthenium states with binding energies of 280.0 and 283.9 eV for Ru3*d*<sub>5/2</sub> and Ru3*d*<sub>3/2</sub>, which corresponds to metallic ruthenium [30, 31]. The spectrum also shows peaks at energies of 281.0, 282.2, 285.2, and 287.9 eV, which correspond to ruthenium in the oxidized state [31] According to XPS data, about 69% of ruthenium is in the metallic state.

The catalytic activity of the Ru/Al–HMS sample obtained was evaluated in the reaction of hydrodeoxygenation of the model compound of bio-oil (furfural) in the presence of water for three varied reaction parameters: temperature, initial hydrogen pressure, and reaction duration.

We examined the influence exerted by the reaction



Fig. 2. XPS Ru3d spectrum of a Ru/Al-HMS sample.

temperature on the conversion and composition of products formed in HDO of furfural in the presence of Ru/Al-HMS (Fig. 3). In the temperature range  $200-300^{\circ}$ C, the conversion of furfural was 100% (2 h, 5 MPa H<sub>2</sub>).

At 200°C, the main products formed in the HDO of furfural were tetrahydrofurfuryl alcohol (THFA, 35%) and cyclopentanol (47%). The reaction mixture also contained methyltetrahydrofuran/tetrahydrofuran (MeTHF + THF, 2%, in aggregate) and mono- and diatomic  $C_4$ – $C_5$  alcohols of varied structure (1,2-pentanediol, 1,5-pentanediol, 2pentanol, n-pentanol, and n-butanol, 9%, in aggregate). It should be noted that the reaction mixture can contain, in addition to alcohols, the corresponding ketones and



Fig. 3. Distribution of products formed in the HDO of furfural (2 h, 5 MPa, G2) at various reaction temperatures in the presence of Ru/Al-HMS catalyst.

aldehydes (cyclopentanone, 2-pentanone, butanal, etc.). However, their total content does not exceed 2%, which is probably due to the large number of acid centers in Ru/Al-HMS, the presence of which is responsible for the predominant formation of alcohols. Presumably, C=O groups are firmly fixed on acid centers of the support, which makes slower the desorption of aldehydes/ketones from the catalyst surface and favors their further conversion into the corresponding alcohols [32]. Compounds obtained as a result of condensation between furfural and(or) half-products formed in the course of HDO (dimers of varied structure, 7%, in aggregate). As the HDO temperature is raised to 250°C, the shares of THFA and cyclopentanol decreased to 27 and 43%, respectively, with the selectivity with respect to tetrahydrofurans and C<sub>4</sub>-C<sub>5</sub> alcohols slightly increasing to 6 and 10%, respectively. The content of condensation products in the reaction mixture increased to 16%. Performing the reaction at 300°C resulted in a sharp increase in the share of tetrahydrofurans to 17% and in that of  $C_4$ – $C_5$  monoatomic alcohols to 36%. The selectivity with respect to pentanols decreased to 2%, which is indicative of a partial deoxygenation of OH groups at 300°C. The selectivities with respect to THFA and cyclopentanol decreased to 7 and 14%, respectively. The share of the condensation products increased to 23%. On the one hand, the formation of heavy oxygencontaining condensation products is an undesirable side process because these compounds can be adsorbed on the active centers of the catalyst and thereby decrease its activity [35, 36]. On the other hand, the condensed furan derivatives can be transformed under the HDO conditions into  $C_{10+}$  alkanes, which can serve as components of the propellant and diesel fuel [37]. Thus, the HDO of furfural in the presence of Ru/Al-HMS in the temperature range 200–300°C yielded a multicomponent mixture of products (C<sub>4</sub>–C<sub>5</sub> alcohols, tetrahydrofurans, cyclopentanol, THFA and condensation products). An increase in temperature leads to active formation of C<sub>4</sub>–C<sub>5</sub> alcohols of varied structure, products of opening of a furan ring, and tetrahydrofurans produced via the hydrogenation of the ring and deoxygenation of the terminal OH group of furfural [13, 38]. Raising the reaction temperature also leads to an increase in the share of condensation products.

It was shown that the initial hydrogen pressure strongly affects the conversion of furfural and the distribution of HDO products (Fig, 4). At a hydrogen pressure of 1 MPa, the conversion of furfural was 29%, with furfuryl alcohol being the main reaction product with a selectivity of 93%. Raising the hydrogen pressure to 3 MPa resulted in that the conversion sharply increased to 95%, with furfuryl alcohol also remaining the main reaction product, but its selectivity decreased to 83%. Other furfural HDO products were detected in minor amounts: THFA, cyclopentanol, pentanediols, MeTHF/THF, and condensation products. If the HDO is performed at a hydrogen pressure of 5 MPa, the conversion of furfural reached a value of 100%, with the reaction mixture mostly containing THFA (35%) and cyclopentanol (47%). The HDO of furfural at a high hydrogen pressure (7 MPa) resulted in a more selective formation of THFA (79%) with the conversion also being 100%. Hence a conclusion can be made that the HDO in the presence of Ru/Al-HMS at a low hydrogen



**Fig. 4.** (a) Conversion of furfural and (b) distribution of products formed in the HDO of furfural (2 h, 200°C) at various initial hydrogen pressures in the presence of Ru/Al-HMS catalyst.

pressure (<3 MPa) leads to a poor conversion of furfural, with furfuryl alcohol selectively formed. As the pressure is raised to 5 MPa H<sub>2</sub>, a full conversion of furfural is reached. However, the reaction occurs simultaneously by several pathways, which is evidenced by te complex composition OF the reaction mixture after the HDO. At high hydrogen pressure (>5 MPa) is predominantly converted in the presence of Ru/Al-HMS to THFA, in agreement with published data on the HDO of furfural in the presence of catalysts based on noble metals [39, 40]. It should be noted, however, that, as regards the industrial applicability, performing the processes at a high hydrogen pressure makes more intricate the design



**Fig. 5.** (a) Conversion of furfural and (b) distribution of products formed in the HDO of furfural (2 h, 200°C) at various reaction durations in the presence of Ru/Al-HMS catalyst.

of industrial installation and requires a gross expenditure of materials and energy [1].

Figure 5 shows the results of the HDO of furfural at various reaction durations. After 0.5 h of the reaction the conversion of furfural was 35%, with furfuryl alcohol being the main product (94%). Tetrahydrofurfuryl alcohol (THFA, 4%) and condensation products (2%) were detected in trace amounts. After 1 h of the HDO, the conversion of furfural was 90%, with the selectivity with respect to furfuryl alcohol decreasing to 54% and that with respect to THFA increasing to 34%. Also, tetrahydrofurans (MeTHF + THF, 2%, in aggregate) and cyclopentanol (1%) were detected in the reaction mixture

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with low selectivities. AS the reaction duration increased to 2 h, the conversion of furfural reached 100%, furfuryl alcohol was not found in the reaction mixture, and the amount of THFA remained at the same level (35%). The selectivity with respect to cyclopentanol substantially increased, to 47%. The products formed in the opening of the furan ring were found in the reaction mixture for the first time: pentanediols (2%, in aggregate) and monoatomic  $C_4$ – $C_5$  alcohols (pentanols and butanol, 7%, in aggregate). As the reaction duration increased further, to 4 h, the selectivity with respect to THFA decreased to 12%, and that with respect to cyclopentanol increased to 62%. In this case, a gradual increase in the selectivity with respect to tetrahydrofurans (MeHTF + THF, 4%, in aggregate) and alcohols ( $C_4$ – $C_5$  alcohols 7%, pentanediols 9%). As the reaction duration increased from 0.5 to 1 h, the content of the condensation products increased to 7%, as the reaction duration was raised further, it remained constant, 6–8%.

Based on the results obtained, we can conclude that the Ru/Al-HMS catalyst we synthesized exhibits a high activity in the HDO of furfural (5 MPa H<sub>2</sub>, 200°C: in 1 h, the conversion of the substrate reaches a value of 90%. In the conditions under study, a double-stage hydrogenation of furfural occurs at short reaction duration to give furfuryl alcohol in the first stage with its further conversion to THFA. At long reaction duration, the conversion of furfural may occur by several pathways (see the scheme). The presence of a small amount of tetrahydrofurans in the reaction mixture suggests that a dehydroxylation/decarbonylation of the THFA being formed can occur on the acid centers of the catalyst to MeTHF and THF, respectively (see Scheme, I) [41]. Also possible is the further opening of the tetrahydrofuran ring, accompanied by the formation of pentanols and butanol; the latter was found in the reaction mixture in amounts not exceeding 1-2%. However, the conversion of THFA by this pathway is a side process, which is evidenced by the low selectivities with respect to tetrahydrofurans and butanol.

In the HDO of furfural in the presence of water on Ru-containing catalysts, alcohols can be formed by another mechanism (see Scheme, II) [42, 43] Originally, pentanediols are formed via opening of the furan ring at  $C_2$ –O or  $C_5$ –O bonds, followed by the hydrogenation of the resulting intermediate to pentanediols with linear or branched chain. Under the HDO conditions, the pentanediols can undergo further stepped deoxygenation to give pentanols and butanols and then also the corresponding  $C_4$ – $C_5$  alkanes.

The opening of the furan ring in the presence of a catalyst having acid centers may also yield cyclopentanol (see Scheme, III) [44, 45]. Furfuryl alcohol undergoes dehydroxylation on acid centers of the support to give furan methyl carbocation. Further occurs a carbocation rearrangement to give an intermediate penta-2,4-diene-1,4-diol. The terminal OH group of the diol is subjected to dehydroxylation. After that the enolic attack on the carbocation center formed after the cleavage of the OH group results in a closure of the ring with its subsequent hydrogenation on metallic centers of the catalyst to give cyclopentanol. According to published data, one of factors determining the nature of the products formed is the strength of interaction between the metal and the furan ring [12]. The strong interaction of furfural with oxophilic ruthenium mostly results in that ring opening products are formed, C4-C5 alcohols, whereas the weaker interaction, e.g., in the case of Pd-containing catalysts, vields furans [46, 47].

## CONCLUSIONS

A study of the fundamental aspects of the hydrodeoxygenation of the model compound of biooil, furfural, in the presence of water on a ruthenium catalyst on Al-HMS mesoporous support demonstrated that the reaction may occur by several pathways: hydrogenation by the scheme furfural  $\rightarrow$  furfuryl alcohol -> tetrahydrofurfuryl alcohol with the subsequent deoxygenation of the OH group to give tetrahydrofurans; hydrogenation with opening of the furan ring to give linear, branched, and cyclic  $C_4$ – $C_5$  alcohols of varied structure. The influence exerted by temperature on the course of the hydrodeoxygenation was examined: in the temperature range 200-300°C, the conversion of furfural is 100%, and the reaction mixture contains tetrahydrofurfuryl alcohol,  $C_4$ - $C_5$  alcohols, and tetrahydrofurans. It was shown that the initial pressure of hydrogen strongly affects the conversion of furfural. Raising the initial pressure of hydrogen within the range 1-7 MPa leads to an increase in the conversion of furfural, with its full conversion reached at 5 MPa.

### CONFLICT OF INTEREST

A co-author, A. L. Maksimov, is the Editor in Chief of Zhurnal Prikladnoi Khimii, the rest of the co-authors state that they have no conflict of interest to be disclosed in the present communication.

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