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Conversion of Methanol to Aromatic-Rich Gasoline over High-Efficiency Bifunctional Catalysts: Green Synthesis of GaZSM-5 Zeolites via Dry-Gel Conversion Strategy

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Abstract—Nanoscale ZSM-5 (AlZ5-D) and Ga-substituted ZSM-5 zeolites ((Al,Ga)Z5-D and GaZ5-D) were synthesized by a green dry-gel conversion strategy. For comparison, ZSM-5 zeolite (AlZ5-T) was also prepared by traditional hydrothermal method. The effects of synthesis method and Ga introduction on the physicochemical property and catalytic behavior of methanol to gasoline (MTG) were studied in detail. The results show that the aromatics selectivity decreased while C_5^+ alkanes selectivity increased for AlZ5-D sample compared with that of AlZ5-T, which was attributed to the significantly reduced density of Brønsted acid sites and weakened strong acid-ity. After Ga introduction, the acid strength of samples further weakened due to the formation of Si–OH–Ga bridge hydroxyl group by insertion of Ga into the zeolite framework, inhibiting the cracking reaction and thus increasing the gasoline selectivity. Moreover, the extra-framework Ga species, especially in the form of GaO⁺ in GaZ5-D sample, exhibited high dehydrogenation activity, leading to the highest selectivity of aromatics and gasoline.

Keywords: ZSM-5 zeolite, nanocrystals, Ga modification, dry-gel conversion, methanol to gasoline

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INTRODUCTION

The conversion of methanol to gasoline (MTG) over solid-acid catalysts is an alternative important pathway for the production of clean fuels due to the richly accessible resources obtained from biomasses, natural gas and coal, which are particularly significant because of the gradual depletion of world-wide crude oil deposits [1, 2]. The gasoline produced by the MTG process mainly consists of aromatics, isoparaffins, naphthenes and olefins [3]. Among these, high value-added aromatics can be used either as a blended composition of gasoline or as the basic feedstock for producing the synthetic materials and fine chemical products in the modern chemical industry [4, 5].

In the past years, researchers have made great efforts to improve the selectivity to gasoline as well as aromatics in MTG reaction. The key technology of catalytic process is the development of high-efficiency catalyst. Owing to the high hydrothermal stability, adjustable acidic property and the shape selective structure for aromatics, ZSM-5 zeolites with particular 10-ring interconnected channel system are widely employed in MTG reaction [6]. However, the mass transfer of reactants, intermediates and product molecules in the micropores (5.1–5.6 Å) of ZSM-5 is limited to some extent, which aggravates the occurrence of secondary reactions and the deactivation of catalysts [7]. Nanoscale ZSM-5 zeolite with short diffusion path length, exhibits remarkably enhanced diffusion ability and larger surface area which expose more active centers, and thus improving the utilization of acid centers in zeolite-catalyzed reactions [8].

In general, nano-ZSM-5 zeolites were synthesized by traditional hydrothermal method using large amount of solvents and organic templates [9]. However, considerable quantities of nitrogen-containing organic wastewater will be generated in the crystallization process, and the posttreatment process is complex, resulting in the energy consumption and environmental problems. At the same time, the product yield is relative low. Since Xu et al. first reported the conversion of aluminosilicate dry gels into MFI-type zeolites [10], the novel method which called dry-gel conversion (DGC) has been extensively applied to synthesize zeolite materials including titanium substituted silicalite-1 zeolites [11], shaped binderless ZSM-11 zeolites [12], aluminophosphate molecular sieves [13], and also mesostructured silica [14]. Unlike the hydrothermal synthesis, there is no direct contact between the dry gel and liquid water during DGC process, which minimizes the waste disposal and makes almost complete conversion of dry gel powder to zeolites with a high yield [14]. In light of these merits, DGC approach is considered as an eco-friendly and cost effective green route for the synthesis of zeolite nanocrystals. Askari and co-workers [15] successfully synthesized the SAPO-34 nanoparticles by DGC method and found that the formation of nanocrystals in the process of dry-gel conversion was because of the high nucleation density and slow crystal growth rate. Niphadkar et al. [16] prepared the Sn-MFI zeolites with similar SiO₂/SnO₂ molar ratio by hydrothermal crystallization and DGC methods, respectively. The activation energy of nucleation (En) and crystallization (Ec) were also measured. Compared to the conventional hydrothermal synthesis, shorter induction period and lower values of En and Ec were observed for DGC method. In addition, Jia et al. [17] demonstrated that higher utilization of template was obtained for the synthesis of ZSM-5 zeolites by DGC route and the prepared catalyst showed higher selectivity to light aromatics and longer catalytic lifetime in the reaction of methanol to aromatics than that of the hydrothermal synthesized samples.

However, the strong acid strength of ZSM-5 zeolite causes the inevitable coke formation, and thus leads to the low stability of catalysts. Ga modification is expected to effectively modulate the catalyst acidity and improve the selectivity to aromatics [18, 19]. The commonly methods of metal modification, such as mechanical mixing and incipient wet impregnation, would result in the surface enrichment of metal components, and thus exhibit poor synergy between the active metal species and acid sites [20]. Additionally, active metal species are easily lost during the reaction, resulting in the insufficient utilization of the catalysts. Isomorphous substitution is considered as an effective method to prepare metal-modified bifunctinal catalysts. Our previous work [21] found that nanoscale Ga-modified ZSM-5 zeolites prepared by hydrothermal isomorphous substitution method showed higher dispersion of active Ga species compared with the post-synthesized samples. Moreover, parts of the Ga atoms were successfully incorporated into the zeolite framework provided weak Brønsted acidity, and thus inhibited the cracking reaction in 1-hexene aromatization.

Hence, in this paper, nanoscale ZSM-5 and Ga partially substituted ZSM-5 zeolite as well as Ga completely substituted ZSM-5 gallosilicate were synthesized by DGC method. For comparison, ZSM-5 zeolite was also prepared by traditional hydrothermal synthesis method. The catalytic performance of synthesized catalysts was evaluated in the MTG reaction. The effect of the textural properties, acidity and the distribution of Ga species on the catalytic performance of MTG reaction was studied in detail.

EXPERIMENTAL

Catalyst preparation. Nano-ZSM-5 zeolite was synthesized by DGC method according to the following procedures: aluminum isopropoxide (AIP) was first dissolved in the mixed solution of tetrapropylammonium hydroxide (TPAOH) and deionized water. Afterwards, tetraethoxysilane (TEOS) was added to the above aqueous solution with a molar composition of 1 Al₂O₃: 100 SiO₂: 35.7 TPAOH : 1083.3 H₂O. The obtained gel was kept for 5 h under agitation and the resulting mixture was transferred to a rundkolben for rotary evaporation followed by drying at 60°C. The DGC crystallization was carried out in a specially stainless-steel autoclave equipped with a self-supporting sand core funnel for loading the dry gel fine powder, and a certain amount of water was placed at the autoclave bottom to provide steam. The autoclave was heated at 180°C for 18 h and the product was dried at 110°C overnight and calcined at 550°C for 6 h to remove the template. The obtained sample was transferred into their H-form by ion exchange method as described elsewhere [22], denoted as AlZ5-D. For comparison, nano-ZSM-5 zeolite was also prepared by traditional hydrothermal crystallization method, named as AlZ5-T. The synthesis process was similar to the preparation of AlZ5-D, expect for that the initial gel was directly crystallized in a Teflon-lined stainless-steel autoclave at 180°C for 24 h.

Ga partially isomorphous substituted ZSM-5 zeolite was synthesized as follows: TPAOH, AIP, Ga_2O_3 , and H_2O were mixed together to obtain the complete dissolution of aluminium source and gallium source. The subsequent process was consistent with the above synthesis of AlZ5-D, except that the crystallization time was 12 h. The molar ratio of the initial gel was 35.7 TPAOH:100 SiO₂:0.57 Al₂O₃: 0.43 Ga₂O₃:1083.3 H₂O. The obtained sample was labeled as (Al,Ga)Z5-D. Ga completely substituted ZSM-5 gallosilicate sample GaZ5-D with molar composition of 35.7 TPAOH:100 SiO₂: 1 Ga₂O₃:1083.3 H₂O in the initial gel, was prepared by the same method applied for (Al,Ga)Z5-D but without the addition of AIP.

Catalyst characterization. X-ray diffraction (XRD) analysis was performed on on a Bruker D8 powder diffractometer using CuK_{α} radiation ($\lambda = 1.5406$ Å). The relative crystallinity was calculated by the integral area in the 2θ range of $22.5^{\circ}-25^{\circ}$. The morphology of samples was recorded on a Hitachi S-4800 scanning electron microscope (SEM). ²⁷Al, ⁷¹Ga and ²⁹Si MAS NMR spectra were performed using a Bruker AVANCE III 400 MHz spectrometer. A selective $\pi/12$ pulse was used for quantitative analysis of ²⁷Al MAS NMR spectra. The N₂ adsorption-desorption isotherms were carried out on a Quantachrome Autosorb-1 automatic surface and porosity analyzer. Temperature-program desorption of NH₃ (NH₃-TPD) were measured in a flow system with a thermal conductivity detector. FTIR spectra of pyridine adsorption were performed on an in-situ infrared spectrometer (Frontier, PerkinElmer). The density of Brønsted and Lewis acid sites was determined after desorption at 150°C. Temperature-programmed reduction (H₂-TPR) was performed using a chemisorption analyzer (AutoChem II 2920, Micromeritics). X-ray photoelectron spectroscopy (XPS) was measured on an ESCALAB 250 spectrometer with an Al K_a radiation source (hv =1486.6 eV).

Catalytic evaluation. The MTG reaction was run in a microscopic fixed-bed reactor at a temperature of 400°C and a pressure of 1.5 MPa in a nitrogen atmosphere. The catalyst was pretreated at 450°C for 2 h, and cooled to the reaction temperature followed by pumping the methanol aqueous solution (50 wt %)



Fig. 1. XRD patterns of the prepared catalysts.

into the reactor. The weight feed rate of methanol was 4.0 h⁻¹. The gas effluents and liquid hydrocarbons were analyzed on a gas chromatograph equipped with a PONA capillary column (50.0 m × 0.2 mm × 0.5 µm). Unreacted methanol (or DME) and water were analyzed by gas chromatograph with thermal conductivity detector and a Porapak Q capillary column (4 m × 3 mm). The methanol conversion, X_{MeOH} , and product selectivity, S_i , were calculated according to the formulas:

$$X_{\text{MeOH}} = \frac{n(\text{MeOH})_{\text{in}} - n(\text{MeOH})_{\text{out}} - 2n(\text{DME})_{\text{out}}}{n(\text{MeOH})_{\text{in}}} \times 100\%,$$
$$S_i = \frac{n_{i,\text{out}}k_{i,C}}{\Sigma n_{i,\text{out}}k_{i,C}} \times 100\%$$

where $n_{i,out}$ was the molar quantity of product *i* and $k_{i,C}$ was the number of carbon atoms in its molecule.

RESULTS AND DISCUSSION

The XRD patterns of all samples shown in Fig. 1 revealed typical patterns of $2\theta = 7.9^{\circ}$, 8.8° , 23.0° , 23.1° , 23.6° , 23.9° and 24.4° , indicating that the synthesized zeolites were pure MFI crystals. The basic structure of ZSM-5 zeolite was kept after the introduction of Ga and no diffraction peaks corresponding to Ga₂O₃ phase were observed in the Ga-substituted samples. This may be attributed to that the Ga species were inserted into the zeolite framework or were highly dispersed. Moreover, the relative crystallinities of AlZ5-T and AlZ5-D samples were comparable, demonstrating that



Fig. 2. SEM images of the prepared catalysts: (a) AlZ5-T, (b) AlZ5-D, (c) (Al,Ga)Z5-D, and (d) GaZ5-D.

the dry-gel conversion method can reach a degree of crystallization equivalent to the sample prepared by the traditional hydrothermal method (24 h) in a shorter crystallization time (18 h). It can also be found that the relative crystallinity increased for the samples modified by Ga isomorphous substitution, especially for GaZ5-D sample, which may be due to the larger particle size of the Ga-substituted samples. The average crystal sizes calculated by XRD patterns were ca. 13 nm and ca .17 nm for the AlZ5-D and GaZ5-D samples, respectively.

Figure 2 showed the SEM images of the synthesized zeolites. The morphologies of ZSM-5 aluminosilicates prepared by different methods were quite different. The AIZ5-T sample exhibited rod-like shape consist of nanocrystals, while the AIZ5-D sample were presented in the form of cylindrical aggregates accumulated by the ultra-fine particles. Moreover, the particle size of AIZ5-D sample was smaller than that of AIZ5-T, consistent with the reports that the sample crystallized by DGC method has a smaller grain size due to its higher nucleation density and slower crystal growth rate [23]. After Ga isomorphous substitution, the samples exhibited spherical agglomerates with nanocrytals and the average signal particle size was

larger than that of AlZ5-D sample, in line with the results of XRD that higher relative crystallinity was obtained for Ga-modified samples.

The ²⁷Al, ⁷¹Ga and ²⁹Si MAS NMR spectra of samples were displayed in Fig. 3. It can be seen from Fig. 3a that an intense signal peak at ca. 54 ppm was observed for all Al-containing ZSM-5 samples, demonstrating that most Al atoms were inserted into the zeolite framework in the form of tetrahedral coordination. A weak resonance peak at about 0 ppm assigning to hexa-coordinated extra-framework Al species was also appeared for these samples. The obvious signal at approximately 160 ppm of Ga-substituted ZSM-5 samples shown in Fig. 3b was belong to the tetrahedral coordinated Ga species in the framework sites. With the increase amount of Ga added in the gel mixture, the content of framework Ga increased significantly. No signals of extra-framework Ga species were observed, which was mainly due to their strong quadrupole effect [24]. The ²⁹Si MAS NMR spectra in Fig. 3c showed that all the samples exhibited two signals at ca. -114 and -104 ppm, respectively. The intense peak signal at -114 ppm was attributed to Si*(OSi)₄ units. The poorly broad peak at approximately -104 ppm was



Fig. 3. ²⁷Al MAS NMR spectra (a), ⁷¹Ga MAS NMR spectra (b) and ²⁹Si MAS NMR spectra (c) of the prepared catalysts.

assigned to (MeO)*Si $(OSi)_3$ (Q₃, Me = Al or Ga) sites. Additionally, it can also be found that the peak signal of Q₃ sites of AlZ5-D sample shifted towards low-field (high frequency) after Ga isomorphous substitution, which was attributed to the insertion of Ga atom into the zeolite framework resulting in a decrease in chemical shielding [25].

The N₂ adsorption-desorption curves of samples

Sample		Surface area, m	² /g	Pore volume, cm ³ /g			
	BET	micorpore	external	total	micorpore	mesopore	
AlZ5-T	472	306	166	0.701	0.122	0.579	
AlZ5-D	505	311	194	0.803	0.141	0.662	
(Al,Ga)Z5-D	470	320	150	0.426	0.136	0.290	
GaZ5-D	474	337	137	0.604	0.135	0.469	

Table 1. Textural properties of the prepared catalysts

were shown in Fig. 4a. All isotherms exhibited the characteristics of type I and type IV isotherms, indicating the coexistence of micropores as well as mesopores in the prepared zeolites. Moreover, it can be inferred from the SEM images that the formation of mesopores was mainly caused by the accumulation of nanocrystallines. Additionally, more intense and steeper hysteresis loop was observed for AlZ5-D sample than that for Ga-substituted ZSM-5 zeolites, which may be attributed to the smaller particle size of AlZ5-D. The BJH pore size distributions of the samples were shown in Fig. 4b. As seen, an obvious pore distribution between 30 and 300 nm was observed for all samples, which came from the capillary condensation within the intergranular mesopores [26].

The corresponding textural data of samples was listed in Table 1. The mesopore volume and external area of AlZ5-D sample were larger than that of AlZ5-T, which was attributed to the smaller particle size of AlZ5-D zeolite. After Ga introduction, the mesopore volume and external area of the zeolites obviously decreased compared with that of AlZ5-D sample, which may be due to the rapid growth after nucleation of nanoscrystallines by Ga isomorphous substitution via dry-gel conversion route, leading to the relative large nanoparticles.

Figure 5 illustrated the NH₃-TPD curves of the synthesized zeolites. All samples exhibited two peaks in the low-temperature (L.T.) of ca. 200°C and the hightemperature (H.T.) of ca. 370°C, which was attributed to the adsorption of NH₃ on weak and strong acid sites, respectively. As observed in Table 2, there was obvious shift towards lower temperature for both the L.T. and the H.T. desorption peak of the AlZ5-D sample, demonstrating that the acid strength of AlZ5-D was weaker than that of AlZ5-T. After Ga introduction, the samples show a further lower temperature of H.T. desorption peak. It should be mentioned that the strong acid sites in zeolites were mainly Brønsted acid sites. Therefore, the reduction of strong acidity was ascribed to the lower $\Delta(\chi O - \chi Ga)$ compared with $\Delta(\chi O - \chi A I)$, where $\chi A I$, $\chi G a$, and χO were the electronegativity of the framework Al, Ga, and O, respectively. Because the smaller difference between yO and xGa, the binding of Ga–O is weaker compared with that of Al-O bond. Therefore, the Si-O(H⁺)-Ga bridging hydroxyl cannot easily give up H⁺, resulting in the weaker



Fig. 4. N₂ adsorption-desorption isotherms (a) and BJH pore size distributions (b) of the prepared catalysts.

Brønsted acidity of Ga-substituted ZSM-5 zeolites [27].

Py-IR measurement was estimated to investigate the density of Brønsted and Lewis acid sites of the samples, and the corresponding data was listed in Table 2. Both the density of Brønsted and Lewis acid sites decreased for the samples synthesized by DGC method compared with the AlZ5-T. This may be due to the fact that parts of extra-framework Al species which did not insert into the zeolite framework during the dry-gel conversion process, was washed away in the subsequent ion exchange process. Moreover, Ga-substituted ZSM-5 zeolites exhibited higher density of Lewis acid sites compared with that of AlZ5-D sample, which can be attributed to the formation of extra-framework Ga species. It can also be found that the density of Brønsted acid sites of (Al,Ga)Z5-D sample was lower than that of GaZ5-D, suggesting the lower total content of metal atoms (Al and Ga) inserted in the skeleton sites because of the competition of Ga and Al.

Figure 6a showed the H_2 -TPR profiles of the prepared samples. A small reduction peak appeared in both samples at ca. 200°C, demonstrating that parts of the low dispersed gallium oxides on the outer surface can be reduced at rather low temperature. Moreover, another characteristic peak at approximately 420°C was also observed, attributing to the reduction of well-dispersed Ga₂O₃ particles formed in the samples. Compared with (Al,Ga)Z5-D, an obvious reduction signal at a higher temperature of ca. 700°C was obtained for GaZ5-D. This was mainly attributed to the formation of cationic GaO⁺ species at charge compensation sites by the replacement of acid protons in

Table 2. Acidic properties of the prepared catalysts

Sample	T_{peak} , ^a °C		Acid amount ^b , µmol g ⁻¹			
2 a	weak	strong	Brønsted acid	Lewis acid		
AlZ5-T	204	381	113.25	84.50		
AlZ5-D	196	373	43.25	35.73		
(Al,Ga)Z5-D	184	364	47.17	56.09		
GaZ5-D	192	368	54.61	71.76		

^a Determined by NH₃-TPD.

^b Calculated by Py-IR.



Fig. 5. NH₃-TPD curves of the prepared catalysts.



Fig. 6. H₂-TPR profiles (a) and Ga 2p3/2 spectra (b) of the prepared catalysts.

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 93 No. 1 2020

Sample	C _{MeOH} , %	Product selectivity, %						C ₄
		C ₁ -C ₄ alkanes	C ₂ -C ₄ olefins	C ₅₊ alkanes	C ₅₊ olefins	Aromatics	%	HTI
AlZ5-T	97.6	34.85	8.59	22.11	4.07	30.38	56.56	0.93
AlZ5-D	97.7	26.20	17.18	33.73	0.38	22.51	56.62	0.91
(Al,Ga)Z5-D	97.2	17.29	21.17	23.74	7.09	30.71	61.54	0.82
GaZ5-D	97.5	17.91	15.35	20.14	7.42	39.18	66.74	0.85

Table 3. Catalytic performance of MTG reaction over the prepared catalysts

GaZ5-D sample, thus leading to the reduction of GaO⁺ at higher temperatures because of the strong interaction between the zeolite framework and GaO⁺ species [28].

XPS spectra were recorded to characterize the Ga species on the zeolite surface. As seen in Fig. 6b, no signal peak was observed for (Al,Ga)Z5-D sample, demonstrating that the content of surface Ga species was very low. In contrast, two types of Ga species were distinguished in GaZ5-D sample with binding energies of ca. 1118.7 and 1120.3 eV, corresponding to Ga₂O₃ particles and active GaO⁺ species, respectively [29], in line with the results from H₂-TPR characterization. The higher binding energy of active GaO⁺ species was attributed to the stronger covalent character of the GaO+/ Brønsted acid coordination center [30]. Because partial electron was transferred from GaO⁺ species to the more electronegative lattice O2- of the zeolite framework, and thus decrease the electron density of GaO+ and result in the higher BEs of Ga 2p3/2 peak.

The catalytic performance over the synthesized zeolites was studied for the MTG reaction and the result was listed in Table 3. The methanol conversion over all the catalysts was above 97%. It is known that there are two distinct but dependent catalytic cycles involved in MTG reaction over ZSM-5 zeolites, which are olefin- and aromatic-based cycles, respectively [31, 32]. The olefinbased cycle is to obtain C₃₊ olefins via the methylation and cracking reaction of low-carbon olefins, while the aromatic-based cycle mainly produce aromatics through continuous methylation and dealkylation reactions of methylbenzene intermediates, which formed by the cyclization and hydrogen transfer reaction catalyzed on Brønsted acid sites. Therefore, the product distributions of MTG on ZSM-5 zeolites can be affected by the different acidity of catalysts. Compared with AlZ5-T zeolite, AlZ5-D sample had a lower density of Brønsted acid sites with weaker acid strength, inhibiting the hydrogen transfer reaction and thus resulting in the lower selectivity to aromatics. Accordingly, the selectivity to C5+ alkanes produced by the competitive reaction was increased. The C_4 hydrogen transfer index (C_4 HTI) calculated by C_4 alkanes divided by the sum of C_4 alkanes and C_4 olefins [33], which was used to describe the extent of the hydrogen transfer process, and the selectivity to lowcarbon C₁-C₄ alkanes as by-products of the hydrogen transfer reaction also decreased. The higher selectivity to light olefins $C_2^{=}-C_4^{=}$ of AlZ5-D sample was attributed to the promotion of olefin-based cycle. Although both cycles process were catalyzed by Brønsted acid sites, the reduction of Brønsted acidity had a more significant effect on the inhibition of the aromatic-based cycle, which in turn promoted the olefin-based cycle.

After Ga introduction, the selectivity to gasoline and to aromatics of Ga-substituted ZSM-5 samples obviously increased compared with that of AlZ5-D. This was due to the fact that although the hydrogen transfer reaction was inhibited by the reduction of Brønsted acidity, the extra-framework Ga species formed in (Al,Ga) Z5-D and GaZ5-D samples substantially promoted the dehydrogenation reaction. Moreover, it can also be found that the selectivity to C_{5+} alkanes decreased while C_{5+} olefins selectivity increased due to the improvement of dehydrogenation process. The highest selectivity to gasoline and aromatics was obtained for GaZ5-D sample prepared by Ga completely isomorphous substitution. This was mainly attributed to the co-existence of extraframework Ga species including Ga₂O₃ and cationic active GaO⁺ species with higher dehydrogenation activity, which significantly promoted the dehydrogenation reaction and thus increased the aromatics selectivity.

In this paper, a green synthesis route via dry-gel conversion method was successfully explored to prepare the nanoscale ZSM-5 (AlZ5-D) and Ga-subtituted ZSM-5 zeolites ((Al,Ga)Z5-D and GaZ5-D) in a shorter crystallization time compared with the traditional hydrothermal method. After Ga introduction, the Brønsted acid strength decreased due to the formation of Si-OH-Ga bridge hydroxyl group, which inhibited the hydrogen transfer reaction. In contrast, the dehydrogenation reaction of cycloolefin intermediates was significantly promoted by the formation of extra-framework Ga species compared with AlZ5-D sample. Ga completely substituted ZSM-5 gallosilicate sample GaZ5-D exhibited the highest aromatics selectivity of 39.18% and gasoline selectivity of 66.74%, respectively, which was attributed to the formation of active GaO⁺ species with high dehydrogenation activity.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest in this work.

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RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 93 No. 1 2020

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