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## BRIEF COMMUNICATIONS

# Selective Conversion of Methanol to *p*-Xylene on Modified High-Silica Zeolites

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**Abstract**—A procedure was proposed for preparation of *p*-xylene from a nonhydrocarbon material, methanol, in the presence of a modified ultrasil. It was shown that ultrasils modified by multiple-charge cations actively catalyze synthesis of xylenes from methanol at atmospheric pressure, and their properties can be controlled by varying the nature, charge, and size, as well as the procedure of introduction of the modifier cation. Modification of H-ultrasil with gallium led to enhanced para-selectivity (70%) of the catalysts, which was attributed to an increase in the ratio of the Lewis to Brønsted acid sites and to a decrease in the effective channel diameters of the zeolite.

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High-silica (HS) zeolites have become the subject of much recent investigation due to their unique catalytic properties, in particular, suitability for catalyzing the synthesis of olefin and aromatic hydrocarbons from a nonhydrocarbon material, methanol [1, 2]. At the same time, the possibility of selective synthesis of *p*-xylene from methanol in the presence of modified HS-zeolites still remains to be explored.

Here, we examined how the nature, concentration, and procedure of introduction of the modifiers affect the acidity and selectivity of high-silica zeolites in the reaction of p-xylene formation from methanol.

## EXPERIMENTAL

The experiments were carried out on a flow-type setup with a fixed catalyst bed (catalyst volume 4 cm$^3$) in a plug-flow reactor at atmospheric pressure in the temperature range 300–450°C. The space velocity of methanol was 2 h$^{-1}$, and the time of the experiments, 0.5 h.

We used a high-silica zeolite of ultrasil type with molar ratio $SiO_2/Al_2O_3 = 61$. The cationic forms of the ultrasil were obtained by the ion-exchange procedure described in [3, 4]. The catalysts modified with 1.0–10.0 wt% gallium were prepared by impregnation of H-ultrasil with a gallium nitrate solution, followed by drying initially in air and subsequently in an oven at 110°C and calcination in a muffle furnace at 550°C for 4 h to achieve the conversion to Ga-H-ultrasil.

The IR spectra were measured on a Spekord spectrophotometer, to which end the zeolites were pressed into thin pellets, 6–8 mg cm$^{-2}$, which were treated in a vacuum for 2 h at 500°C prior to adsorption [3]. Adsorption of pyridine was carried out at room temperature and atmospheric pressure of saturated vapor. The adsorption examinations followed the technique described in [5].

As known, the methanol conversion on zeolite-containing catalysts proceeds by the following scheme [1]:

$$\text{Methanol} \longrightarrow \text{Dimethyl ether} \longrightarrow \text{Olifins} \xrightarrow{H_2\ \text{redistribution}} \text{Isoparaffins and aromatic hydrocarbons}$$

In the temperature range 350–400°C, the degree of methanol conversion is 100% both for the initial Na-form of zeolite and the ion-exchanged zeolite samples. The main products of methanol conversion are olefin $C_2$–$C_4$ (30–40%), aliphatic $C_{5+}$ (15–20%), and aromatic $C_6$–$C_{10}$ (25–40%) hydrocarbons. The yield of $C_6$–$C_8$ aromatic hydrocarbons depends on the nature and concentration of the modifying metal (Fig. 1).

Study of the activity of the catalysts in methanol conversion to aromatic hydrocarbons shows that, along with the H-form, various cationic modifications of ultrasil exhibit the catalytic activity as well. The Na-form of ultrasil is inactive, like in other reactions [6]. Replacement of $Na^+$ by $H^+$ and $M^{n+}$ cations leads to formation of active contacts (Fig. 1).

Like with other types of zeolites [3, 4], on changing from $M^{2+}$-ultrasil with small cations to samples with larger $M^{2+}$ cations, all other characteristics being the same, the activity of the contacts in formation of aromatic hydrocarbons decreases (relative to Mg-, Zn-, and Sr-ultrasils). At the same time, this activity increases on changing from $M^{2+}$-ultrasil to the samples with larger $M^{3+}$ cations (Ho-, Ga-ultrasils against Mg-, Zn-, and Sr-ultrasils). This is evidently due to a high polarizability of $Ho^{3+}$ and $Ga^{3+}$ cations. As seen from Fig. 2, the samples of ultrasil with larger cations exhibit a higher para-selectivity as well.

Among the samples examined, the highest para-selectivity was displayed by Sr- and Ga-ultrasils. However, in formation of aromatic hydrocarbons the Sr-form is much less active than Ga-ultrasil. As known, one of the ways of chemical modification of high-silica zeolites is via introduction of various substances into the zeolite structure channels, which causes the effective diameter of these channels to decrease, and thereby, leads to lower acidity and activity of catalysts in ionic-type reactions [6].

It is seen from Fig. 3 that introduction of gallium by impregnation of the zeolite with an aqueous solution of gallium nitrate, followed by decomposition of the salt at 550°C, caused significant modification of the properties of the catalysts: Their activity decreased, and the selectivity toward *p*-xylene, increased. The reason is that the impregnation of H-ultrasil with a gallium salt solution involves an exchange of a part of $H^+$ ions for $Ga^{3+}$ ions or $Ga(OH)_2$, resulting from hydrolysis of the gallium salt. Upon decomposition of the salt this results in formation of diaspore GaOOH capable of disproportionation into $GaO^+$ and $GaO_2$ ions [5]. The resulting GaO ions can be exchanged by the $H^+$ ions of the Brønsted acid sites, and the $GaO^{2-}$ ions are localized around the B-sites. During calcination, a part of the GaOOH phase can be converted to gallium oxide $Ga_2O_3$ [6], which can be spread over the external surface and inside the pores of zeolite, thereby partially blocking the active sites. This leads to decreases in the protonic acidity and activity of the catalyst in the carbonium-ion type reactions, as well as to modification of the diffusion and adsorption characteristics of the zeolites, which are closely related to their para-selectivity.

Indeed, modification with gallium affects the catalytic and physicochemical properties of H-ultrasil. Introduction of 1.0–10.0 wt% gallium into the H-ultrasil composition causes its para-selectivity to increase. The optimal gallium concentration providing for good yields of xylenes (16.5 wt%) and high selectivity toward p-xylene (70%)

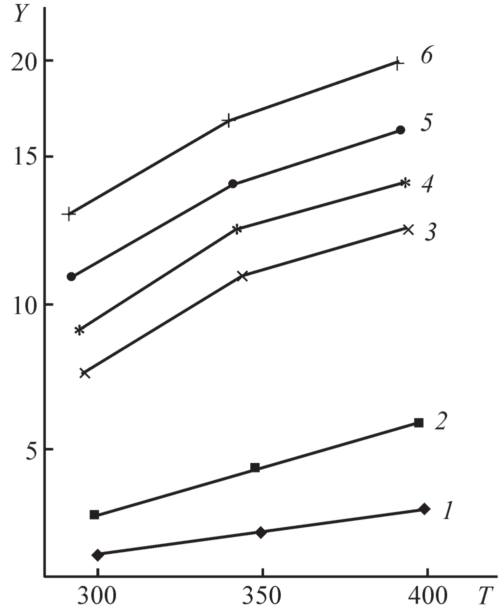

**Fig. 1.** Influence of the nature of the exchange cation on the yield *Y*, %, of $C_6$–$C_8$ aromatic hydrocarbons in methanol conversion in the presence of ultrasils (υ = 2 $h^{-1}$). (*T*) Temperature, °C. (*1*) Na-ultrasil; modifier content, wt%: (*2*) 0.83 Sr, (*3*) 0.70 Zn, (*4*) 0.68 Mg, (*5*) 0.73 Ho, and (*6*) 0.66 Ga.

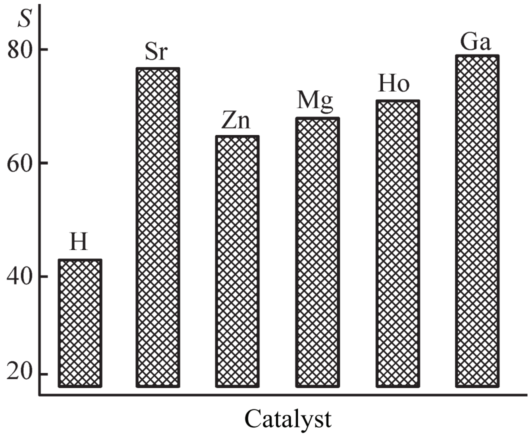

**Fig. 2.** Influence of the nature of catalyst on the selectivity *S*, %, toward *p*-xylene (*T* = 400°C, υ = 2 $h^{-1}$). Modifier content, wt%: H 0.81, Sr 0.78, Zn 0.70, Mg 0.68, Ho 0.73, and Ga 0.66.

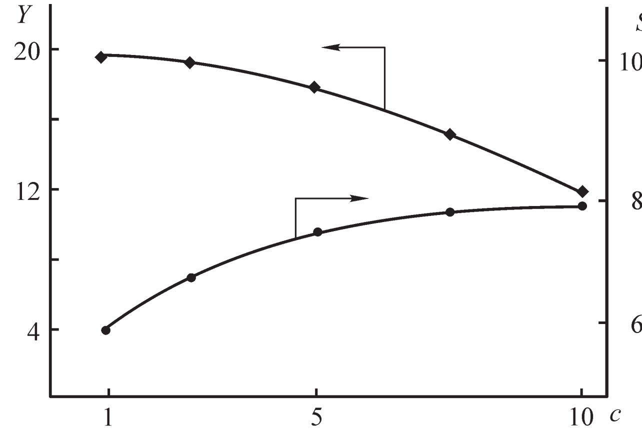

**Fig. 3.** Yield *Y*, wt%, of xylenes and selectivity *S*, %, toward *p*-xylene ($T = 400°C$, $\upsilon = 2$ h$^{-1}$) vs. gallium concentration *c*, wt%.

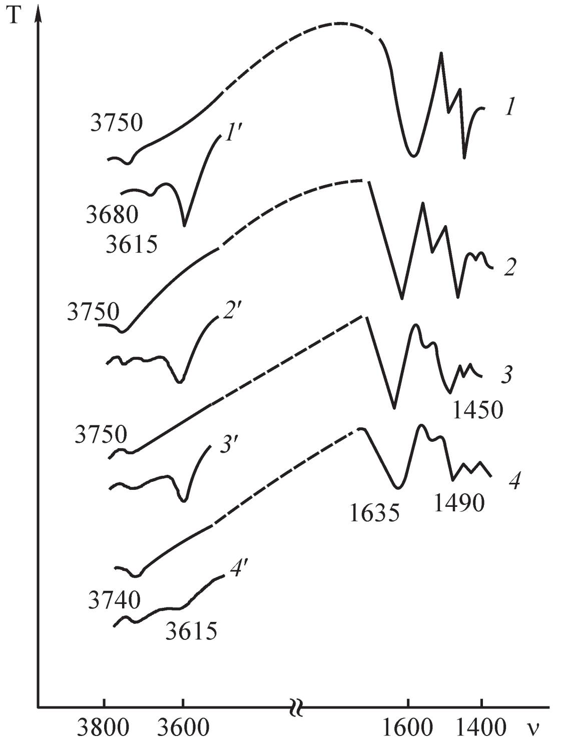

**Fig. 4.** IR spectra of (*1*) H-ultrasil sample and (*2–4*) gallium-modified ultrasil samples vacuum-treated at 500°C for 2 h. (T) Transmission and (ν) wavenumber, cm$^{-1}$.(*1'–4'*) IR spectra after pyridine adsorption at 200°C for 1 h and desorption at 300°C.

is 5.0 wt%. A change in the activity and para-selectivity of the ultrasil, caused by its modification with gallium, is due to decreases in sorption capacity and concentration of strong Brønsted acid sites of the samples. The table shows that, with increasing gallium content in the samples, their sorption capacity with respect to n-heptane and benzene tends to decrease.

Adsorption of n-heptane and benzene vapors on the gallium-modified ultrasil

| Sample no. | Gallium concentration, wt% | Adsorption capacity, cm$^3$ g$^{-1}$ | |
|---|---|---|---|
| | | *n*-heptane | benzene |
| 1 | 0 | 0.164 | 0.08 |
| 2 | 3.0 | 0.132 | 0.068 |
| 3 | 5.0 | 0.105 | 0.060 |
| 4 | 10.0 | 0.082 | 0.047 |

The IR spectra of H-ultrasil and gallium-modified ultrasil samples, presented in Fig. 4, show that the band at 3615 cm$^{-1}$, observed in the region of stretching vibrations of bridging OH groups exhibiting strongly acidic properties, is preserved in the spectra or all the samples, but its intensity tends to markedly decrease with increasing gallium content in the sample. Modification of H-ultrasil with gallium leads not only to a smaller number of strong acid sites but also to a more pronounced change in the ratio of B- to L-sites. This is probably one of the main factors responsible for a change in the catalytic activity, caused by modification of the catalysts with gallium.

## CONCLUSION

Chemical modification of H-ultrasil with gallium leads to an increase in the Lewis to Brønsted acid site ratio and to a decrease in the adsorption capacity of the zeolites, thereby increasing the selectivity of the catalyst toward p-xylene.

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