

# A novel method for the synthesis of hierarchical ZSM-5 zeolite in proton form

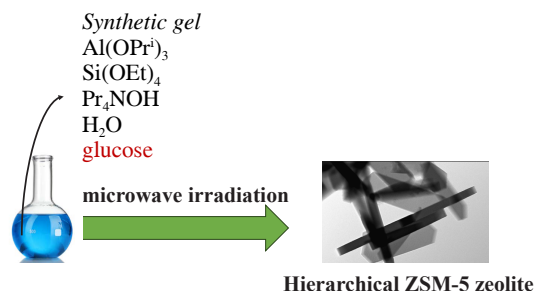
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The synthesis of hierarchical zeolite ZSM-5 in proton form using glucose under microwave irradiation is reported for the first time. The obtained materials were studied by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, N<sub>2</sub> sorption and thermal desorption of ammonia. The hierarchical zeolite ZSM-5 in proton form has predominantly contained weak acid sites; the mesopore volume and total pore volume were 0.5 cm<sup>3</sup> g<sup>-1</sup> and 0.58 cm<sup>3</sup> g<sup>-1</sup>, respectively.



**Keywords:** hierarchical ZSM-5 zeolite, hydrothermal microwave synthesis, biotemplate, proton form, glucose, micro/mesopores, interparticle porosity.

Zeolites ZSM-5 are crystalline aluminosilicates possessing a three-dimensional system of micropores of 0.5–0.6 nm in size,<sup>1</sup> which are used in hydrocarbon and biomass processing technologies.<sup>2–13</sup> However, because of the micropores size in the ZSM-5 structural type zeolite, there are diffusion limitations<sup>14–17</sup> for the catalytic processes using ZSM-5 zeolites. The way to resolve this problem is to synthesize and use the hierarchical ZSM-5 zeolites<sup>18</sup> containing mesopores (intra- or intercrystalline<sup>19</sup>) in catalysis.

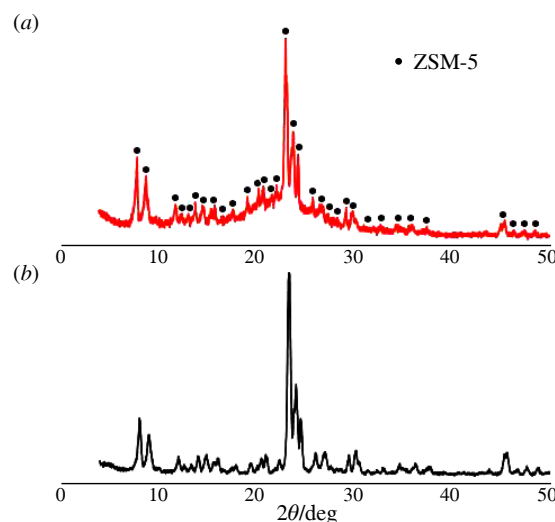
Most of the known methods for obtaining hierarchical ZSM-5 zeolites are represented by two large groups: top-down and bottom-up.<sup>17</sup> The bottom-up concept is a synthesis strategy that, in addition to the main template for forming the ZSM-5 zeolite structure, uses a second template to form mesopores. The second template is typically cetyltrimethylammonium bromide or block copolymers (P123, F127). These compounds must be synthesized separately. Moreover, they are quite expensive. Currently, the so-called ‘green’ synthesis of hierarchical zeolites is being developed, which includes the use of a bioavailable organic compounds<sup>20,21</sup> as a second template. One of such compounds is glucose.<sup>22–26</sup> The synthesis of *b*-axis oriented crystals of ZSM-5 zeolite is an extremely important goal for the creation of effective catalysts. This is due to the fact that the straight channels in the ZSM-5 zeolite are located parallel to the *b*-axis. Thus, the reduction of the size in the *b* direction allows one to reduce diffusion limitations and improve properties of the catalysts in such processes as the conversion of methanol to propylene.<sup>24–26</sup> However, to date, the synthesis of *b*-axis oriented crystals of ZSM-5 zeolite is a labor-intensive, multi-stage process, resulting in the preparation, as a rule, of the zeolite in the sodium form. Therefore, an urgent task is to develop effective methods for the synthesis of hierarchical ZSM-5 zeolites directly in proton form using glucose as a second template.

In this work, we report for the first time the synthesis of a hierarchical ZSM-5 zeolite in the proton form using glucose as a second template under microwave irradiation.<sup>27</sup> Tetra-*n*-

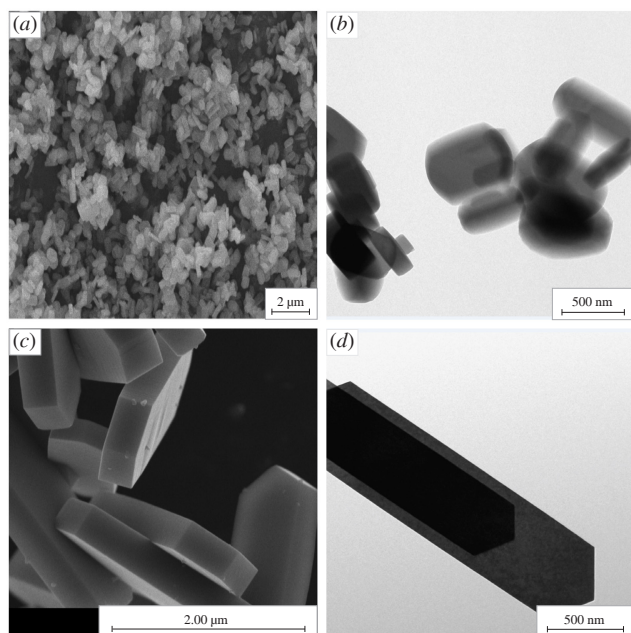
propylammonium hydroxide was employed as a first template needed for ZSM-5 structure.

The X-ray diffraction patterns of ZSM-5 zeolites synthesized with addition of glucose (HZSM-5-G) and without addition of glucose (HZSM-5) are presented in Figure 1. The prepared samples were ZSM-5 zeolites, according to the ICDD database, which has been confirmed by the presence of the characteristic peaks in the 2 $\theta$  ranges of 8–9 and 23–25° in the patterns.

The particles of HZSM-5 zeolite synthesized without adding glucose have not exceeded 1  $\mu$ m in size and have the shape of a three-dimensional hexagon [Figures 2(a),(b)]. The addition of glucose at the synthesis stage made it possible to obtain crystals oriented in the *b* direction with dimensions of 3.5  $\mu$ m  $\times$  1  $\mu$ m  $\times$  400 nm, which was in a good agreement with literature data.<sup>24</sup>

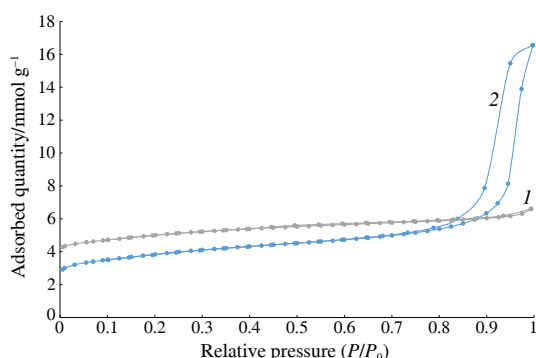


**Figure 1** XRD patterns of synthesized zeolites: (a) HZSM-5 and (b) HZSM-5-G.



**Figure 2** SEM and TEM images of the synthesized zeolites: (a), (b) HZSM-5 and (c), (d) HZSM-5-G.

The  $N_2$  adsorption–desorption isotherms of the synthesized zeolites are presented in Figure 3. The isotherm of HZSM-5 corresponds to IUPAC type I, which is common for the microporous HZSM-5 zeolite. The isotherm of HZSM-5-G has a hysteresis loop indicating the presence of hierarchical structure in the material due to the intercrystalline mesoporosity. The characteristics of the specific surface area and porous structure of the prepared hierarchical HZSM-5-G and HZSM-5 zeolite synthesized without addition of glucose are given in Table 1. The specific surface area of mesopores, total pore volume and volume of mesopores of HZSM-5-G are dramatically increased compared with the conventional sample. The presence of mesopores confirms the formation of a hierarchical structure in the obtained HZSM-5-G sample. Mesopore volume and total pore volume of the HZSM-5-G sample were 0.5 and 0.58  $\text{cm}^3 \text{g}^{-1}$ , respectively. These values have significantly exceeded similar indicators of the samples synthesized by conventional hydrothermal synthesis,<sup>24–26</sup> where the mesopore volume and total pore volume were 0.24 and 0.3  $\text{cm}^3 \text{g}^{-1}$ , respectively.



**Figure 3**  $N_2$  adsorption–desorption isotherms at 77 K for the (1) HZSM-5 and (2) HZSM-5-G.

**Table 1** Textural properties of the synthesized HZSM-5-G and HZSM-5 zeolites.

Sample	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	$S_{\text{meso}}/\text{m}^2 \text{g}^{-1}$	$V_{\text{total}}/\text{cm}^3 \text{g}^{-1}$	$V_{\text{micro}}/\text{cm}^3 \text{g}^{-1}$	$V_{\text{meso}}/\text{cm}^3 \text{g}^{-1}$
HZSM-5-G	311	118	0.58	0.08	0.5
HZSM-5	425	77	0.23	0.13	0.1

**Table 2** Acidic properties of HZSM-5-G and HZSM-5 zeolites.

Sample	Centers of weak and medium strength <sup>a</sup> / $\mu\text{mol g}^{-1}$	Strong acidic centers <sup>b</sup> / $\mu\text{mol g}^{-1}$	Total acidity/ $\mu\text{mol g}^{-1}$
HZSM-5-G	55	40	95
HZSM-5	60	58	118

<sup>a</sup> Calculated as the amount of  $\text{NH}_3$  ( $\mu\text{mol g}^{-1}$ ) desorbed below 300 °C.

<sup>b</sup> Calculated as the amount of  $\text{NH}_3$  ( $\mu\text{mol g}^{-1}$ ) desorbed above 300 °C.

The acidic properties of the synthesized samples were determined via the temperature-programmed desorption of ammonia (Table 2). All samples have a bimodal distribution of acid centers by strength: weak and strong acid centers, respectively. Adding glucose at the synthesis stage resulted in the decrease in the total acidity to 95  $\mu\text{mol g}^{-1}$  compared to that of the sample synthesized without the addition of glucose (118  $\mu\text{mol g}^{-1}$ ). The number of strong acidic centers decreases, while the number of weak acidic centers remains virtually unchanged. Therefore, the addition of glucose at the synthesis stage allows one to adjust the ratio of weak and strong acidic centers.

Thus, the hierarchical ZSM-5 zeolite in the proton form was synthesized for the first time using glucose as the second template under microwave irradiation. The hierarchical HZSM-5 zeolite has been prepared by one-stage crystallization for 2 h. It was found that glucose addition at the synthesis stage makes it possible to obtain zeolite ZSM-5 *b*-axis oriented crystals with the thickness of 400 nm; the mesopore volume and the total pore volume of the sample were 0.5 and 0.58  $\text{cm}^3 \text{g}^{-1}$ , respectively. Adding glucose at the synthesis stage allows one to regulate the acidic properties: weak acid sites are predominating in the synthesized hierarchical zeolite HZSM-5. The physicochemical properties of the obtained material make it a promising catalyst for various acid–base processes in petrochemistry, oil refining and organic synthesis.

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#### Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7852.

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