

## SYNTHESIS AND THEIR TEXTURE CHARACTERISTICS OF MESOPOROUS SILICA GEL AS SURFACTANT SUPPORTING RUTIN

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**ABSTRACT:** Mesoporous silica sorbent samples ordered at 30÷80°C were synthesized using the surfactant rutin using sol-gel technology. Based on the sorption of benzene vapors on sorbents, their texture and sorption properties were studied. According to it, it was determined that the specific surface area ( $S_{BET}$ ) of the sorbents is 675,6÷514,5 m<sup>2</sup>/g, and the average diameter of the pores is equal to 5,3÷32,8 nm.

**KEYWORDS:** sol-gel, rutin, surfactant, mesoporous sorbent, specific surface area, sorption capacity.

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### INTRODUCTION

Among the nanomaterials, mesoporous silica and composite materials based on it are important due to their ordered pores and high specific surface area [1-2]. Mesoporous silica materials are used in many fields due to their high thermal and mechanical stability, environmental safety, as well as the possibility of modification with metal oxides and monomers with different functional groups [3-6].

At present, porous silica and composite materials based on it, such as MSM-41 (MSM - Mobile Composition of Matter) and SBA-15 (Santa Barbara Amorphous) are widely available [7-8]. Hundreds of different representatives of these two classes of mesoporous silica materials have been obtained by changing the synthesis conditions, controlling the pore size, and modifying them with monomers with different functional groups, polymers, and oxides of variable valence metals [9-12].

The initial synthesis of a new generation of mesoporous MCM-41 silicon materials with the same size pores was carried out in the early 1990s by the US company Mobil Oil [13]. In 1992, this US company synthesized ordered mesoporous M41S type adsorbents belonging to the MSM-41 family for use as sorbents [14-16].

Zhao and his colleagues [17] synthesized SBA-15 materials with hexagonal cylindrical mesopores with a size of 30 nm using R123 (Pluronic acid,  $\text{EO}_{20}\text{-PO}_{70}\text{-EO}_{20}$ ) triblock copolymer as an amphiphilic surfactant in an acidic environment. SBA-15 is a siliceous material consisting of ordered cylindrical and parallel mesopores with a wall thickness of  $0,3\div 0,6$  nm. SBA-15 has a large specific surface area ( $S_{\text{BET}}$ ,  $600\div 1000$   $\text{m}^2\cdot\text{g}^{-1}$ ), having mesopores with an average diameter of  $2\div 30$  nm and a large volume ( $2,5\div 3$   $\text{cm}^3\cdot\text{g}^{-1}$ ), as well as chemical inertness, ecological it is better than MCM-41 in terms of safety, thermal and hydrothermal stability. Therefore, various representatives of SBA-15 are widely used in obtaining heat-protective coatings, separating individual genes in genetic engineering, transporting drugs, creating chemical sensors, heterogeneous catalysis, obtaining adsorbents with high sorption capacity, alternative energy, and electronics [18-20].

## EXPERIMENTAL SECTION

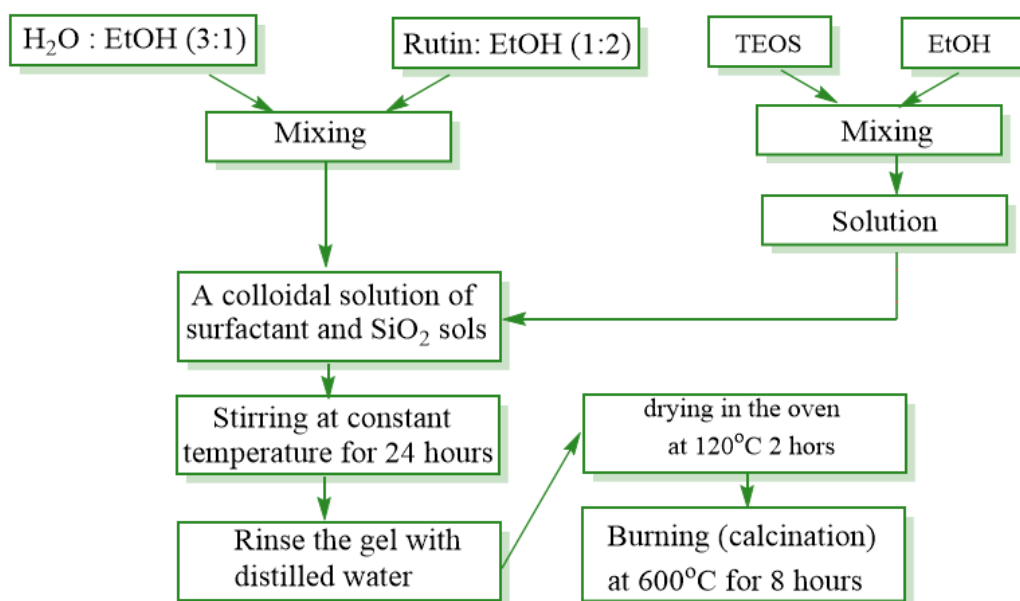
### Materials and methods

In the synthesis of mesoporous silica sorbents, TEOS- $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$  (Jinan Xinggao Chemical Technology Co., Ltd, China, purity>98.6%) was used as a source of  $\text{SiO}_2$ , and recycled ethyl alcohol (purity>96.2%) was used as a solvent. An alcoholic solution of the surfactant rutin flavanoid (purity>98.6%) was used to control the structure and size of the pores. A 0,1M solution of  $\text{CH}_3\text{COOH}$  ( $K_d=1,8\cdot 10^{-5}$ , pH=5,2) was used during the synthesis process to control the catalyst and solution environment. During the synthesis, the solution environment was monitored using a Mettler Toledo FP-20 pH meter. The textural characteristics of the sorbents were studied by the adsorption of benzene vapors at 298 K using a Mac-Ben-Bakra sensitive quartz spiral setup. The surface morphology of the sorbents was studied by scanning electron microscopy. Elemental analysis of the sorbents was performed using a detector (EDS Aztec Energy Advanced X-Act, Oxford Instruments) attached to a SEM EVO MA 10 (Carl Zeiss, Germany) scanning electron microscope.

### Synthesis of silica sorbents

1. 10 ml of alcohol solution containing rutin was added to 100 ml of water-alcohol (3:1) mixture. The solution was then mixed by adding 5 mL of a 0,1M solution of  $\text{CH}_3\text{COOH}$ . 10 ml of an alcoholic solution containing TEOS was added dropwise to the solution over 30 minutes. 4. The resulting colloidal solution was placed in a thermostat and stirred at a constant temperature for 24 hours, that is, until a gel was formed. 5. The resulting gel was washed several times with distilled water. 6. Samples were dried at  $105^\circ\text{C}$  for 4 hours. 7. Porous mesoporous sorbent samples were obtained by calcination (calcination step) at  $500^\circ\text{C}$  for 8 hours in a dry powder calcination furnace (Witeg, GmbH, Germany).

The synthesis of mesoporous SBA-15 sorbents was carried out according to the following scheme.



## RESULTS AND DISCUSSION

Isotherms obtained from the sorption of benzene vapors on sorbents obtained at different temperatures are presented in Figure 1-a.

It was observed that the sorption isotherms of benzene vapors on sorbents taken at 30°C rise sharply up to the relative pressure  $p/p_0=0,2$  and approach the saturation state at  $p/p_0=0,9$ . It can be seen that adsorption and desorption lines merge to form a hysteresis loop at  $p/p_0=0,4\div 0,8$  due to capillary condensation of vapors of adsorbed substances. From this, the sorbent consists of mesopores, and the adsorption isotherm is the basis for saying that it belongs to the IV type according to the IUPAC classification.

The sorption isotherms obtained from the sorbents synthesized at 50°C and 80°C showed saturation of the monolayer as the relative pressure increases to  $p/p_0=0,25$  approaching the saturation state at  $p/p_0=0,9$ . An increase in the size of the hysteresis loops formed by the merging of the adsorption and desorption lines indicates that the mesopores in them are larger.

The graph  $p/p_0/a(1-p/p_0)=f(p/p_0)$  was drawn according to the isotherms obtained from the sorption of benzene vapors to the sorbents, and it was found to correspond to the linear equation of BET ( $R^2=0,9812$ ) (Fig. 2b) .

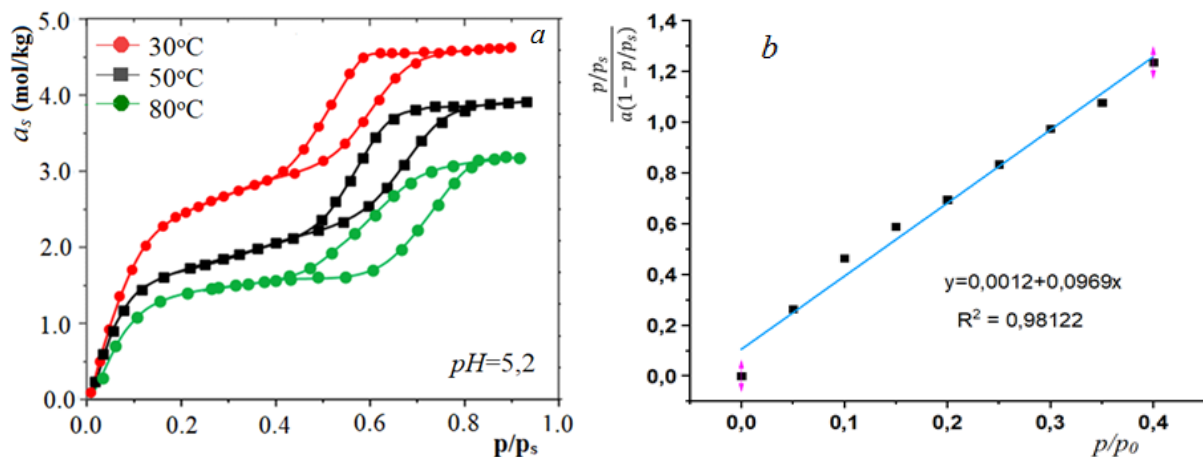


Figure 1. Sorption isotherms for benzene vapors on sorbents obtained at different temperatures and their correspondence to the BET linear equation

Adsorption isotherms and textural characteristics of sorbents using the BET equation: specific surface area ( $S_{\text{BET}}$ ,  $\text{m}^2/\text{g}$ ), average pore diameter ( $D$ , nm), monolayer capacity of sorbents ( $a_m$ , mol/kg) and saturation adsorption ( $a_s$ , mol/kg) were calculated (table).

Table 1. Textural characteristics of sorbents obtained at different temperatures

Fusion temperature, °C	$S_{\text{BET}}$ , $\text{m}^2/\text{g}$	$a_m$ , mol/kg	$D$ , nm	$a_s$ , mol/kg
30	$675,6 \pm 15$	$1,3 \pm 0,7$	$5,4 \pm 0,05$	$5,3 \pm 1,2$
50	$589,2 \pm 10$	$1,6 \pm 0,5$	$18,6 \pm 1,18$	$4,2 \pm 0,6$
80	$514,5 \pm 15$	$1,2 \pm 0,3$	$32,4 \pm 8,24$	$3,8 \pm 0,4$

From the table, it can be seen that with increasing temperature, the specific surface area of the synthesized sorbents decreases, and the maximum diameter of the pores increases. It was also observed that 24,5% of benzene vapors adsorbed in sorbents obtained at 30°C, 38,1% and 31,5% in sorbents obtained at 50°C and 80°C, respectively, were adsorbed to the monolayer. Calculation results revealed that 96,5% of the total number of pores in the sorbents obtained at 30°C, and 84,6% of the sorbents obtained at 80°C are mesopores.

The surface morphology and elemental composition of the sorbents were studied in a SEM EVO MA 10 (Carl Zeiss, Germany) scanning electron microscope (Figure 2).

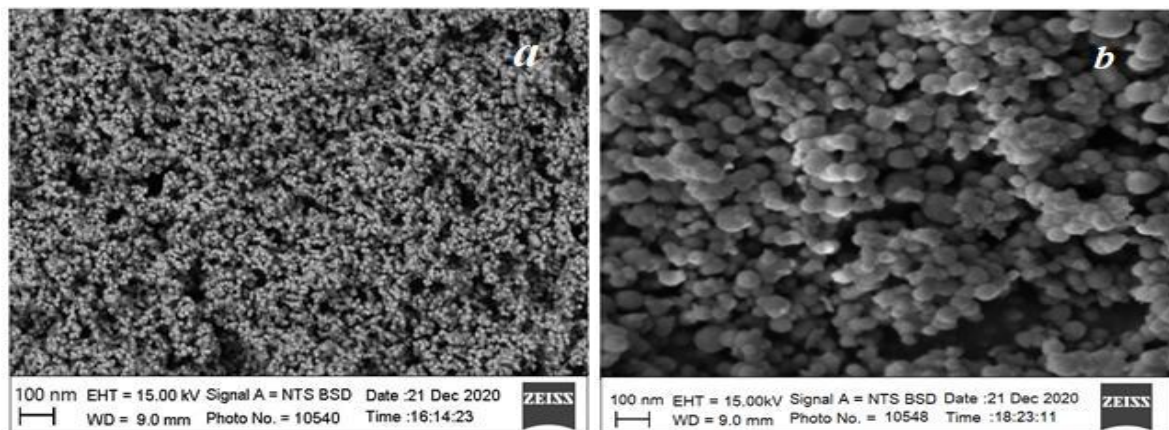


Figure 2. Sorbents obtained at 30°C (a) and 50°C (b).

#### SEM image of the surface

From the SEM images, it can be seen that the pores of the sorbents obtained at 30°C and 50°C are evenly distributed on the surface and they are the same in size. From this, it can be said that the surface of the sorbents is monodispersed and consists of spherical SiO<sub>2</sub> nanoparticles of the same size.

In the sorbents obtained at 30°C, with increasing temperature, it can be seen that porosity and their orderly arrangement on the surface are slightly disturbed (Fig. 3a). The EDS analysis of the sorbents shows that the quantitative ratio of the elements in their composition corresponds to the amount of the initial precursor (Fig. 3b).

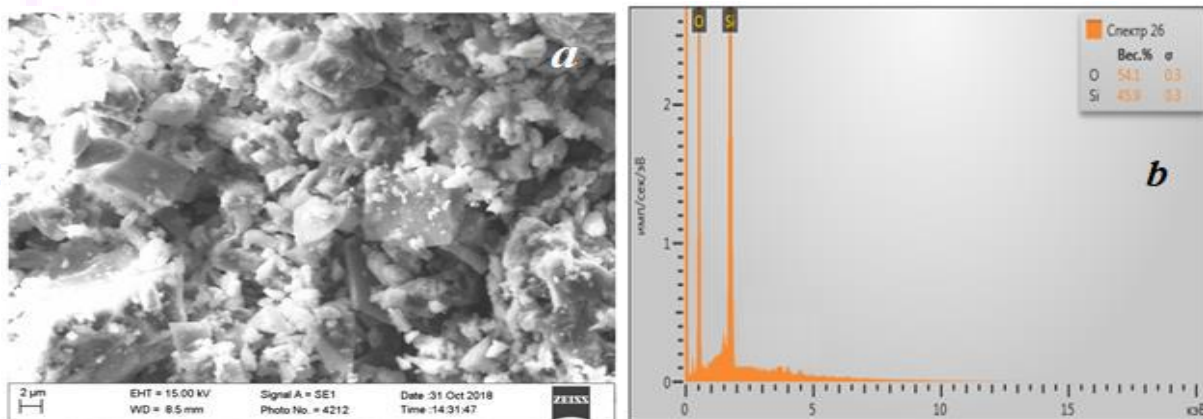


Figure 3. SEM (a) and EDS (b) images of the sorbent taken at 80°C

Also, the phase composition of the sorbents was studied using an X-ray diffractometer from Empyrean, Malvern Panalytical (Germany). The resulting diffractograms were analyzed semiquantitatively using calibration standards (Figure 4).

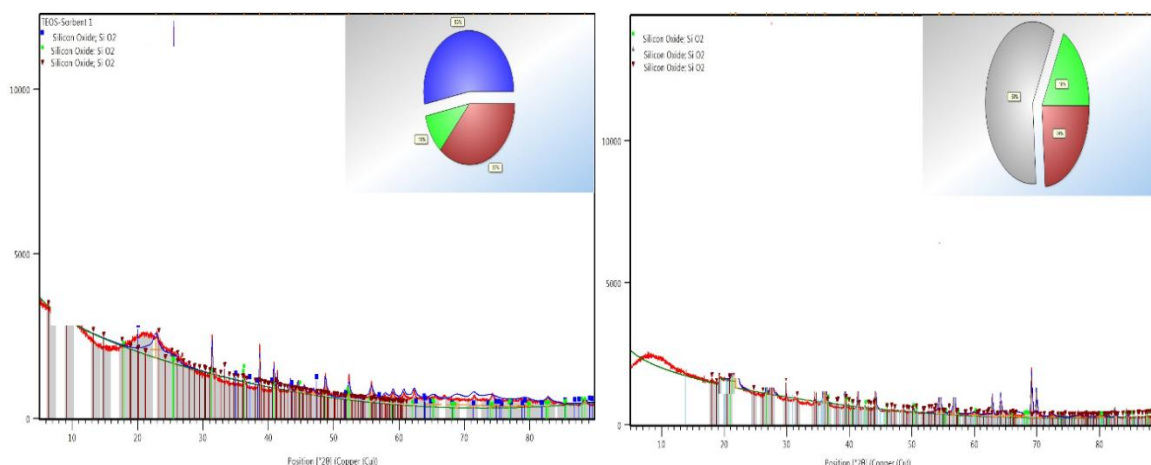


Figure 4. Phase composition of sorbents obtained at 30°C and 50°C

From the figure, it can be seen that amorphous SiO<sub>2</sub> consists of dense weak signal spectra in the fields from  $2 = 18,1^{\circ} \div 82^{\circ}$ . This indicates that the sorbents consist of an amorphous phase composition.

### CONCLUSIONS

The effect of temperature on the texture characteristics of silica (SiO<sub>2</sub>) sorbents obtained by sol-gel technology, the average surface, average diameter of pores was studied. According to it, when the temperature is increased from 30°C to 80°C during the synthesis, the average pore diameter (D) of the sorbents increases from 5,3 to 32,8 nm, and the specific surface area (S<sub>BET</sub>) increases from 675,6 to 514,5 m<sup>2</sup>/g. was observed to decrease up to From the SEM analysis of the surface morphology of the sorbents, it was found that the pores are evenly distributed on the surface and they are uniform in size. Also, EDS and X-ray diffractometric analysis of sorbents revealed that their phase composition and quantitative ratio correspond to the quantitative composition of the initial precursor.

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