The analyses of the parameters of microporous structure in metal-oxide nanomaterials by comparative sorption methods

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Abstract. The article is concerned with the investigation of nanomaterials based on SiO₂ and SnO₂ obtained with the use of sol-gel technology. The specifics of applying the comparative adsorption methods for studying such porous structure parameters of nanomaterials as micropores volume are discussed.

1. Introduction
Recently the adsorption methods of analyses are among the most popular methods for studying the porous structure parameters in nanomaterials [1-3]. As recommended by IUPAC, the porous systems are classified by predominant pore size into microporous (pore diameter up to 2 nm), mesoporous (2 to 50 nm), and macroporous (over 50 nm). Recently the micropores are additionally classified into ultramicropores and supermicropores with a boundary between them of about 1 nm. At the same time only ultramicropores (<1 nanometers) are considered as "the true microporous" where the special mechanism of volume filling with a phase change of an adsorbate from a status of the adsorbed gas in the condensed phase without the intermediate education mono- or a polymolecular layer operates on walls of pores. Supermicropores are intermediate between the "true" micropores and mesopores, here the formation of the condensed layer on a surface of pore walls can precede a phase change.
In metal oxide sensors [4, 5], the macropores can facilitate the feed of gas or liquid materials to nanoreactors, as well as carry away the reaction products. The micropores appear to be a key player in adsorption processes of semiconducting gas sensors. In mesh structures, there is a microporous system that blocks and unblocks the conductivity. That is why the measurement of micropores volume in metal-oxide nanomaterials is an actual problem.

2. Experiment
In this study the sol-gel technology [6, 7] was used to synthesize the porous nanomaterials based on silicon dioxide and stannic oxide. Tetraethoxysilane served as a source (precursor) of silicon dioxide, and inorganic water-soluble tin salt SnO₂·2H₂O was used as a source of stannic oxide. The propyl and butyl alcohols served as solvent. To obtain powders, 10 % aqua ammonia (NH₄OH) was added to the solutions-sols. Adding ammonia is accompanied by changes in pH of the solution ranged from 2 to 8, and an immediate condensation of the hydrolysis products takes place resulting in a much faster gelation process. After the gelation, evaporation of the solvent at the indoor temperature was performed, and then the powders received were heat-treated for 30 minutes at the temperature of 600 °C.
To control properties of the synthesized nanomaterial surface, the nitrogen thermal desorption and atomic force microscopy were used. Specific surface area and pore distribution measurements were made using Sorbi MS (CJSC «META», Novosibirsk, Russia). Before the measurements, all samples...
were pretreated in the SorbiPrep sample preparation station. The operating principle of the station is based on the degassing dispersed and porous materials by heating in a stream of an inert gas (helium). The station allows you to set the temperature and time of heating in the range of 50–400° C, 0–99 minutes.

3. Results and discussion
For the measurement of external surface area and the volume of micropores it is necessary to use the comparative methods of analyses. In general terms the sorption equation looks like:

\[ a(h) = a_{\mu}(h) + S\alpha(h) + a_{id}(h) \]  

(1)

The first member of sum describes sorption in the micropores, the second one describes sorption in the mesopores and the last one shows the capillary condensation contribution. The specific surface of macropores is very small (from 0.5 to 2 m²/g), so the adsorption on the surface of the pores of this type can essentially be neglected.

For the nitrogen when relative pressures are less than 40 % (when capillary condensation doesn’t take place), the equation looks like follow:

\[ a(h) = V_{\mu} + S\alpha(h), \]  

(2)

where \( V_{\mu} \) is a value of the micropores volume, \( S \) is the specific surface area of mesopores, \( \alpha(h) \) – unit-area adsorption. This is a linear equation, and it can be presented as a straight curve. The value of \( V_{\mu} \) can be found as cut-off of approximate line in the axis of ordinate, the value of \( S \) – from the slope of the curve. For the pattern without micropores this curve passes through the origin.

In the figure 1 examples of evolution of the data obtained by the instrument Sorbi, in coordinate a-\( \alpha \) are given.

![Figure 1. Typical a - \( \alpha \) dependences for samples containing and not containing micropores](image)

The line I in the figure 1 corresponds to the standard sample of Al₂O₃ without micropores, the line II corresponds to the sample with microporous system. The volume of micropores in the samples like II is calculated on a ratio:

\[ V_{\mu} = k\cdot b, \]  

(3)

where \( b \) is the value which is split off by the line II on ordinate axis, \( k \) is a constant depending on the ratio of density of an adsorbate in gas and liquid phases (for nitrogen value of \( b = 0.00015 \)).

For investigation a set of metal-oxide patterns preheated in various conditions before the measurements was chosen. For all the patterns the thermal desorption measurements were made using Sorbi MS. For example figure 2 presents the adsorption isotherms for a set of samples with composition 0.85SiO₂-0.15SnO₂ and 0.5SiO₂-0.5SnO₂ preheated in SorbiPrep in various conditions.
Figures 2. Adsorption isotherms for a set of samples: 1 – 0.85SiO\textsubscript{2}-0.15SnO\textsubscript{2} without pretreating, 2 – 0.85SiO\textsubscript{2}-0.15SnO\textsubscript{2} with pretreating at 150°C, 40 min, 3 – 0.50SiO\textsubscript{2}-0.50SnO\textsubscript{2} without pretreating, 4 – 0.50SiO\textsubscript{2}-0.50SnO\textsubscript{2} with pretreating at 150°C, 40 min

Figures 3, 4 illustrate $a$ - $\alpha$ dependences based on the analyses of adsorption isotherms shown in the figure 2.

Figure 3. Two $a$ - $\alpha$ dependences for the samples with composition 0.85SiO\textsubscript{2}-0.15SnO\textsubscript{2}

Figure 4. Two $a$ - $\alpha$ dependences for the samples with composition 0.50SiO\textsubscript{2}-0.50SnO\textsubscript{2}

From the figures 3, 4 it can be seen that the samples number 2 and 4 which were not preheated in SorbiPrep station are characterized by microporous system with volume 0.011 cm\textsuperscript{3}/g for 0.85SiO\textsubscript{2}-0.15SnO\textsubscript{2} sample and 0.009 cm\textsuperscript{3}/g for 0.5SiO\textsubscript{2}-0.5SnO\textsubscript{2} sample. Most likely, this is driven by H\textsubscript{2}O molecules removal from the porous structure during the thermal annealing. The parameters of porous structure, including the specific surface area (S) and external surface area (STSA) are shown in the table 1.
From the table 1 it can be seen that heat treatment of samples 1-4 at T = 150 °C and t = 40 min in SorbiPrep station leads to the microporous system release. Such preheating conditions were chosen for all other samples as optimal. It was noticed that the presence of a system of micropores is observed only in the samples of composition with molar share of silicon dioxide more than 0.5. The maximal specific surface area is 403 m²/g for 0.85SiO₂-0.15SnO₂ sample and 225 m²/g for 0.5SiO₂-0.5SnO₂ sample. However, for gas-sensitivity it is necessary to obtain the layers with high content of solid-state phase [4]. These samples were also investigated and the results are presented in table 1.

4. Conclusions
In result, it was found that the most important parameters that influence on microporous system appearing are mole ratio of the components and time-temperature conditions of preheating the patterns before the measurements. In some cases it was noticed that microporous system can be found in the patterns after longstanding preheating. The study of metal oxide nanomaterials by comparative sorption methods allows us to confirm the assumption of the existence of a multilevel system of pores in the gas-sensitive layers, and to develop the technological regimes for obtaining of the layers for gas sensors of new generation with the most advanced characteristics, where the surface development and the presence of multilevel porous system plays a decisive role.

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