Surface modified silica gels and an express method for determination of their specific surface area

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Abstract: *Silica gels are one of the most widely used adsorbents. The best view of the properties of silicas as catalytic supports, adsorbents and other applications give the adsorption-texture parameters and especially the specific surface area. Hydrated silicon dioxide is amorphous ($SiO_2.nH_2O$),a reactive compound with various contains. Due to the serious practical interest of the determination of the specific surface area of materials many methods are developed and have found application. The study evaluates the impact of the surface and surface modification on the possibility of an express method for determination of specific surface areas of silica gels.*

Keywords: *SILICA GELS, ADSORPTION, POROSITY, TEXTURE PARAMETERS.*

1. Introduction

Silica gels with high adsorption properties are widely used for humidity control, filtration of liquids and solution, separation in multicomponent solution, as a catalyst for various catalytic reactions for the manufacture of butadiene from ethanol (feedstock for the synthetic rubber production etc. The possibility of silica gel to absorb many substances from the liquid phase is used in the industrial cleaning of various oils, oil removal from polymeric and resinous substances, sulfur compounds cleaning etc.

Due to the serious practical interest of the determination of the specific surface area of materials many methods are developed and have found application. Various methods are based on nitrogen adsorption, mercury porometry, calorimetric, gas-chromato-graphical, filtration, microscopic measurements etc. Modern technologies helped the development and the improvement of these methods and they have found application depending on their benefits and disadvantages [1-3]. However, the application of the adsorption methods for specific surface area determination is still the most reasonable method in the practice.

On Table 1 are given the main practically applied adsorption methods [4, 5].

Table 1: *Adsorption methods for determination of a specific surface area*

Most applied adsorption methods	Rarely used adsorption methods	Adsorption methods applied in some cases
Two-parametric equation of BET	Langmuir	Ross-Olivier
Empirical methods: *t*-, α_S-, n(C_{BET}) -graphics	Dubinin-Radushkevich-Kaganer	Frenkel, Halsey, Hill
	Frenkel, Halsey, Hill	Huttig
	Innes	Harvey

By the mechanism of polycondensation the following transformation occurs.

$$nSi(OH)_4 \rightarrow Si_nO_{2n-m} + (2n-m).H_2O$$

The process of polycondensation leads to colloid particles formation with size between 20 ÷ 200 Å. Drying of hydro gel of silicon acid, structural net of joining sphere particles remains. Due to the increasing of the number of particles and formation of strong chemical bonds, formation of SiO_2 skeleton of the materials occurs. During the drying process of the silicon acid the structural “network” of joined spherical particles remains.

As a result of increasing the number of particles and achieving strong bonds between them the silicon-oxide skeleton is formed.

Although the empirical methods: t-, α_S-, n(C_{BET})-graphics use the best laboratory practices for the simultaneous determination of the external surface (specific surface, and the micro pores volume, the two-parametric equation of Brunauer-Emmett-Teller (BET) theory for polymolecular adsorption is the basis of the standard methods for determining the specific surface of the materials [6].

The method of liquid phase adsorption may be used for determination of the specific surface area of the porous materials. In that case, the adsorption isotherms are obtained by subjection of the determined amount of the explored material to the solution of a well absorbing substance - absorbent. The adsorption value is determined by changing the solution concentration. For determining the specific surface area dyes are widely used as adsorbents because of their higher adsorption possibility compared to the corresponding solvents. As a result after monolayer formation from the dyes molecules the solvent is completely displaced from the surface. A typical case is chemically modified silica surfaces or physically modified structures.

During the first half of the 20th century was shown the important role of the hydroxyl groups on the silica surface regarding the adsorption of molecules with dipole and quadrupole moments. Increasing the concentration of the hydroxyl groups on the silicas surface (by hydratation) leads to higher energy of adsorption of these molecules.

All authors report that the using methods for determining the specific surface are labor intensive and are characterized by a long time of holding. The mentioned is referring to most modern automated equipment company "Micromeritics. This requires using express methods for the specific surface determination of various materials. The most difficult problem is determining the range of method validity by comparison with the received results for the same sample and widely practically used methods. In this way the influence of the specific surfaces can be evaluated as well as the influence of the modification of the surfaces, determined by the express methods. A selective toluene adsorption was used as an espress method. The object of our research was silicas with different specific surfaces. A Klyachko-Gurvich method, having acceptable accuracy, was chosen as a method of comparison.

The aim of this research is to determine the specific surfaces of the silicas with different specific surfaces with or without chemically modified surfaces and also of these with physically modified structure. To compare the values of the specific surfaces with those obtained for the same samples using the "Klyachko-Gurvich" method [7]. Determine the limits of validity of the express method used.

2. Experimental

1. Samples

1.1 Silicas and carbon silica gels

Carbon silica gel product consists of silicon acid, precipitated on an active carbon with high adsorption capacity to organic materials. Five type of Russian commercial silica gels were used for the aim of our study, which differ in their particles size distribution and their porosity, denoted as КСК1, КСК2, КСК2а, КСК2,5, KCK3 : Carbon silica gels are synthesized according to the procedure described in [8]: The samples are denoted as ACSG-1 and ACSG-2.

2. Characterization of the samples

2.1 The bulk density of the samples is determined

2.2. Measurement of the specific surfaces of the samples

2.2.1 Selective adsorption of toluene in a mixture with isooctane.

The test specimens (fraction 0.25-0.50 mm) are thermally treated at (453 - 573 K) for 2 hours, after which the specimens weighing about 1 g are placed in tubes and exactly 2 ml (mixture 40 % toluene and 60% isooctane) is poured from the microburette. The refractive index of the initial mixture determined with the Abbe refractometer must be in the range 1.4328-1.4330. The adsorption equilibrium was established after 3 hours. The refractive index of the solution is then determined. Usually 2-3 parallel measurements are performed with one sample, and then they are averaged.

2.2.2 Determination of the specific surface with Express equipment for determination by the one-point method of Klyachko - Gurvich.

For the purposes of the study, calibration on an etalon- silica gel with a surface of ~ 280 m^2/g was used. Before each measurement, the samples were dried at 383 K for 2h.

2.2.3. Obtaining of the silica gels

Precipitation of amorphous silica from alkaline silicates with mineral acids. Silicon raw material is Na-silicate and sodium acid H_2SO_4. The process can be described with the following reaction:

$$Na_2O.3SiO_2 + H_2SO_4 = 3SiO_2 + H_2O + Na_2SO_4$$

Silica gels are characterized by a corpuscular structure: their pores are formed between their primary particles having spherical shape globules. When packed tightly the fine globules form a structure of finely porous silica gel, while the large globules in the "loose" packing have the structure of the porous silica gel. Important characteristic of the silica gels is their bulk density. In the porous cells it varies in the region between 0.4 ÷ 0.5 g/cm^3, whereas for the fine porous silica gels from 0.7 ÷ 0.8 g/cm^3.

Chemical modification of the surface of silica gels is one of the ways to change their adsorption properties and can be done by different groups introducing – amino, sulfonic groups, fluorine atoms, and etc. That is mainly connected with the OH- groups replacing or their combinations with different reactives, which strongly alters the hydrophilic character by replacing the OH- groups from the silica gel surface with H-atoms leading to production of hydrogen silica gel and polysiloxane hydride.

2.1. Method of preparation

Carbon silica gels were synthesized as follows: Technical water glass, diluted with 50 ml water, to 4,1% SiO_2 was mixed with 0,8 g active carbon (AC with 0,08 – 0,125mm size particles), and then dried to the constant mass at 383-388 K. The ratio permits to obtain one of the most active carbon silica gel with 10% mass of carbon black. The compound was mixed for 30 min, and then threatened with HCl to acidity pH~4.5.

Mixing continues to the beginning of coagulation. Then gel leaves to maturation in the excicator for 2-3 days. After that gel was milled into particles and dried by following conditions: 2-3 days at standard temperature 25^{o}C and then dried at 313-393K to humidity 75-80%. After drying the sample was washed with water in order to eliminate Cl- ions, and then dried again at 313-393 K for 60-70 h. The obtained gel was activated at 513 ÷525 K in a porcelain crucible with a cover.

3. Results and Discussion

Table 2: *Basic technological parameters of the samples*

Sample	Granulometric composition, mm	Bulk density, g/cm^3	Mass,g
KCK1	0.25-0.50	0.40	1.0019
KCK2	0.25-0.50	0.40	1.0018
KCK2a	0.25-0.50	0.42	1.0027
KCK2,5	0.25-0.50	0.46	1.0040
KCK3	0.25-0.50	0.51	0.9933
ACSG-1	0.25-0.50	0.79	1.015
ACSG-2	0.25-0.50	0.79	1.038

Table 2 shows the main technological parameters and specific surfaces of the samples, determined by selective adsorption of toluene and the reference method. It can be seen from the table that the bulk density of the samples varies in a wide range of 0.40 - 0.80 g/cm^3. The samples with the lowest bulk density are usually with the lowest specific surface area, and those with the highest bulk density KCK3, ACSG-1and ACSG-2 are with the highest specific surface area 550-750 m^2/g determined by the CAT method and the Klyachko-Gurvich reference method (Table 3).

The values of specific surfaces determined by the Selective adsorption of toluene (SAT) method and their comparison with those obtained by the reference method are presented in Table 3.

Table 3: *Specific surface of the samples*

Sample	n_o^{20}	A, Gurvich-Klyachko determined	A, determined by SAT method,m^2/g
KCK1	1.4303	272	235
KCK2	1.4288	308	281
KCK2a	1.4298	338	349
KCK2,5	1.4290	373	379
KCK3	1.4270	473	553
ACSG-1	1.4263	758	612
ACSG-2	1.4264	742	603

The sample KCK3 characterized with a bulk density of 0.51 g/cm^3 has a specific surface area of 473 m^2/g, sample ACSG-1 and ACSG-2 with a bulk density of 0.79 g/cm^3 and specific surface area of 758 m^2/g and 742 m^2/g, respectively. From the data obtained it was established correlation between the bulk density and the specific surface area for the silica gels and carbon silica gels samples, determined by the Klyachko-Gurvich method.

The specific surface differs for the samples KCK2, KCK2a and KCK2,5 from those determined by Klyachko-Gurvich method and the difference is less than 10%. They have a typical bulk surface in the range of 0.40-0.46 g/cm^3 and a specific surface area between 300-400 m^2/g. It can be noted that, with one exception of KCK1 sample, the difference is as mush greater as the highest specific surface area was determined (Table 3) by the Klyachko-Gurvich method (KCK3 ACSG-1, ACSG-2). For these samples, the bulk density is the highest (0.5-0.8 g/cm^3) compared to those of the other samples. Sample ACSG-1 (characterized by the highest bulk density) has the highest specific surface area.

3. Conclusion

As a results of our investigation and the results obtained of the specific surface determined by Klyachko-Gurvich method, it can be concluded that for the samples with specific surface area over 500

m^2/g, for all chemical modified samples the selective adsorption method of toluene with isooctane is practically inapplicable. So we consider that a definitive conclusion can be drawn after further studies on a large group of modified silica gels with a very low and very high specific surface area with different types of porous texture.

3. References

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