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LAWS OF SYNTHESIS OF SILICA GELS WITH MOLECULAR-SIEVE PROPERTIES

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Influence of conditions at all stages of silica gel synthesis on the formation of structure with molecular-sieve properties was investigated. It was shown that the conditions promoting formation of such structure, are: the minimum rate of the reaction of silicon acid gel polycondensation, minimum duration of recondensation processes, maximum value of capillary compression forces at drying and constant dehydration speed.

Досліджено вплив умов на всіх стадіях синтезу сілікагелю на формування структури з молекулярно-ситовими властивостями. Показано, що умовами, які сприяють утворенню такої структури, є мінімальна швидкість реакції поліконденсації гелю кремнієвої кислоти, мінімальна тривалість процесів переконденсації, максимальна величина сил капілярного стиснення під час сушіння та стала швидкість дегідратації.

Исследовано влияние условий на всех стадиях синтеза силикагеля на формирование структуры с молекулярно-ситовыми свойствами. Показано, что условиями, способствующими образованию такой структуры, являются минимальная скорость реакции поликонденсации геля кремниевой кислоты, минимальная продолжительность процессов переконденсации, максимальная величина сил капиллярного сжатия при сушке и постоянная скорость дегидратации.

Statement of purpose

Adsorbents, blank substrates for catalytic active substances and catalysts that have not only the definite chemical composition and the surface nature, but also porous structure are necessary for various industrial processes.

Efficiency of gas mixes adsorption separation, as well as productivity and selectivity of catalysts are appreciably connected with character of porosity [1].

Now the increasing attention is paid to the elaboration of methods of porous materials synthesis – carbon and zeolite molecular sieves with the developed specific surface, considerable sorption volume and uniformly sized micropores [2].

Interest to such materials is connected with a problem of accumulation of hydrogen, natural gas clearing, separation of gas mixes, drying of gases, etc.

To solve these problems ultramicroporous silica gels, possessing molecular-sieve properties and having diameter of pores less then 0,7 nm may also be successfully used.

Origination of porous materials of different structure is a step to the expansion of branches of their practical use in adsorbtion technology and catalysis.

Analysis

Silica gel is one of the most studied adsorbents.

The great possibilities of its porous structure regulation have defined wide usage of micro- and macroporous silica gels in the processes of adsorption and catalysis [3; 4].

Despite a considerable number of the researches devoted to the silica gel structure, investigation of structurization mechanisms and influence of various factors on its porous structure and adsorbtion properties, regular researches devoted to the laws of ultramicroporous silica gels synthesis are practically absent.

Synthesis of silica gel is a multistage process that includes formation of silicon acid sol and its transition in hydrogel, hydrogel ripening and aging, washing out from reaction side products, removal of excessive moisture and hydrogel transformation into xerogel, therefore porous structure of an end-product depends on conditions of carrying out of each stage.

Purpos

The purpose of the given work was the investigation of conditions at all stages of synthesis on structure formation of silica gels with molecular-sieve properties, and also clarification of the most important factors promoting formation of silica gels with molecular-sieve structure.

Experimental

Objects of research in the given work were microporous silica gels which were obtained, using the most conventional way which included interaction of solutions of liquid glass and sulfuric acid with sol formation, transition of sol in gel, washing out from reaction side product – sulphate of sodium and drying in which result hydrogel passes in xerogel, and at all stages of synthesis various conditions (pH, SiO_2 concentration, temperature, etc.) were changed.

Adsorbtion properties of samples were investigated by the weight adsorbtion method in the vacuum Mac-Ben-Bakr equipment with quartz spring scales.

Adsorption isotherms were processed by the equations of the BET theory and the theory of micropores volume filling of Dubinin-Radushkevich [5]. The diameters of a pores were determined by the molecular probes method. As the adsorbates H_2O (diameter of molecules d = 0,32 nm), CH_3OH (d = 0,44 nm), C_6H_6 (d = 0,57 nm), CCl_4 (d = 0,69 nm) were used.

At the stage of gel formation value of pH of sol (from 1 to 7), concentration C of SiO_2 in sol (from 3,0 to 10,4 % mass), temperature T (from 280 to 453 K) were varied and also gel formation in a thin layer *l* (to 10 mm) was studied. The results of research are presented in tab. 1.

As it is shown from the table increasing of pH, concentration of SiO_2 and temperature leads to the reduction of time of gel formation, but does not affect on the silica gel porous structure: at different pH of sol in the acid medium, concentrations of SiO_2 and temperatures silica gels are received that have approximately identical values of a specific surface area S_{sp}, limiting sorption volume of pores V_S and practically not adsorb CCl_4 vapour, that is they have molecular-sieve properties. Silica gels, received from sols with pH > 5 which have pores with d > 0,69 nm make an exception to what considerable sorption of CCl_4 vapour testifies.

Table 1

Influence of gel formation conditions on the silica gel porous structure

Conditions of gel formation		Time of gel formation, h	CH_3OH S_{sp}, m^2/g	CH_3OH V_S, cm^3/g	CCl_4 V_S, cm^3/g
pH (C= 8 % mass, T=293 K)	1.0	26	590	0.22	0.004
	2.0	22	630	0.24	0.01
	2.5	8	620	0.23	0.01
	4.0	0.5	600	0.24	0.01
	5.0	0.08	630	0.24	0.04
	5.6	0.03	640	0.25	0.15
	6.1	0.008	630	0.26	0.20
C, % mass (pH=2, T=293 K)	3.0	190	640	0.23	0.04
	4.6	100	630	0.24	0.01
	5.2	72	640	0.23	0.02
	7.0	43	610	0.22	0.02
	10.4	16	630	0.24	0.01
T, K (pH=2, C=8 % mass)	280	92	590	0.21	0.03
	318	2.67	610	0.22	0.02
	338	1.33	610	0.22	0.04
	373	0.58	600	0.22	0.01
	453	0.2	630	0.23	0.07
l, mm (pH=2, T=293 K, C=8 % mass)	3	–	1000	0.50	0.004
	6	–	1010	0.54	0.002
	8	–	980	0.39	0.003
	10	–	950	0.40	0.005

Some features are clarified during the process of gel formation in a thin layer. In this case the structure is formed that is characterised not only by molecular-sieve properties, but also a high specific surface area (≈1000 m^2/g) and high enough sorption volume of pores (0,40–0,50 cm^3/g). Possibly, in such conditions because of increasing of rate of formation of three-dimensional structure of gel small aggregates of primary parts of sol are formed that are densely packed.

At the stage of washing out of silicon acid hydrogel from a reaction side product (sodium sulphate) influence of pH, washing water temperature and washing out duration t of hydrogel received from sol with pH=2, on xerogel porous structure were studied. Results are presented in tab. 2.

Table 2

Influence of conditions of washing out on the silica gel porous structure

Conditions of washing out			CH_3OH			CCl_4 V_S, cm^3/g
pH	T, K	t, h	S_{sp}, m^2/g	V_S, cm^3/g	E_0, kJ/mol	
2.0	303	2	600	0.25	14.6	0.01
		24	630	0.21	–	0.01
4.0	303	2	640	0.25	14.6	0.02
		24	620	0.22	15.5	0.01
5.3	303	2	580	0.26	14.3	0.05
		24	640	0.23	15.1	0.17
7.0	303	2	520	0.21	13.3	0.09
		24	650	0.27	12.9	0.21
2.0	303	1	630	0.24	–	0.02
		5	700	0.29	–	0.02
	323	1	630	0.25	–	0.03
		5	7000	0.26	–	0.06
	343	1	640	0.26	–	0.04
		4	740	0.29	–	0.17

It is shown from the obtained results that for formation of silica gels with molecular-sieve structure it is necessary hydrogel washing out by water with pH ≤ 5 and T ≤ 323 K.

Increase of pH, temperature and also of washing out duration leads to more adsorbtion capacious silica gels formation to what increasing of sorption volume of pores at adsorbtion of CCl_4 vapours and reduction of characteristic energy of adsorption E_0 testifies. It can be connected with aging processes.

For studying of influence on porous structure of duration of aging the hydrogel received from sol with pH=2, before washing out left to age at a room temperature throughout different time (till 33 days). The obtained results have shown that silica gels which aged till 20 days are microporous, but their pores are accessible to molecules CCl_4 and only from not aging hydrogel silica gel with molecular-sieve properties is formed.

The important stage in the process of silica gel synthesis is the drying stage during which under the influence of capillary forces the hydrogel is strongly compressed and final formation of silica gel structure takes place. At this stage influence of temperature and dehydration kinetics on porous structure was studied. For research the hydrogel was used received from sol with pH=2 and washed out by water with pH=2. Results are presented in tab. 3.

Table 3

Influence of conditions of drying on the silica gel porous structure

T, K	CH_3OH				CCl_4 V_S, cm^3/g
	S_{sp}, m^2/g	V_S, cm^3/g	W_0, cm^3/g	E_0, kJ/mol	
293	720	0.27	–	–	0.11
303	720	0.31	0.19	12.3	0.16
313	700	0.29	–	–	0.15
333	750	0.32	0.21	12.8	0.18
353	740	0.32	–	–	0.18
363	690	0.30	0.21	12.6	0.23
378	760	0.32	0.19	12.2	0.23
393	720	0.32	–	–	0.19
423	700	0.29	0.18	13.0	0.19
443	730	0.31	–	–	0.20
463	730	0.32	0.20	12.6	0.19
293, air flow	670	0.26	0.19	14.5	0.01
303, air flow	650	0.23	–	–	0.004

It is shown from the table drying in the interval of temperatures 293–463 K allows to receive microporous silica gels which pores, however, is available to molecules CCl_4. Only air flow drying leads to structure formation of silica gels with molecular-sieve properties. Investigation of silica hydrogel dehydration kinetics has shown that at all temperatures dehydration process has two periods on speed of moisture removal – constant and decreasing speed, and only drying in air flow occurs at constant dehydration speed. Possibly under such conditions uniform contraction of the gel skeleton in result of uniform removal of moisture from an evaporation zone is provided.

The experimental data obtained during the research of influence of various conditions at all synthesis stages on silica gels – molecular sieves formation, it is possible to explain on the basis of silicon dioxide globular structure theory and formation and rebuilding of its skeleton mechanisms [3; 6–9].

At the stage of gel formation the basic chemical process is reaction of polycondensation of the silicon acid, leading to formation of hydrosol particles and conditions of carrying out of this stage influence on the reaction rate, but do not affect on the size of particles: in a wide interval of pH (from 1 to 5), concentrations of SiO_2 in sol (from 3,0 to 10,4 % mass) and temperatures (from 280 to 453 K) silica gels with molecular-sieve properties are received.

At a stage of washing out of silicon acid hydrogel occurs not only removal of sodium sulphate, but also aging of hydrogel which consists in rebuilding of hydrogel skeleton in result of processes of carrying over SiO_2 which lead to growth of globules. As in the basis of recondensation processes reaction of siloxane bonds formation and decomposition lies process of rebuilding of a skeleton increases at duration and temperature increasing, and also at deviation of pH of medium from an isoelectric point (pH≈2) to which the minimum rate of formation of bonds Si–O and the least solubility of silicon dioxide in water solutions corresponds.

At the drying stage aging of hydrogel continues and its contraction under the influence of capillary forces proceeds. Thus influence of temperature on the porous structure of xerogel is shown in the rate change of globules growth, formation and fortifying of contacts between them in result of recondensation processes, and also in changing of capillary pressure forces which tighten the hydrogel skeleton.

The dominant role in formation of silica gel with molecular-sieve structure at this stage belongs to the dehydration rate that defines uniformity contraction of hydrogel skeleton.

Conclusion

Silica gels with molecular-sieve properties are such microporous adsorbents which pores diameter is commensurable with diameter of molecules and does not exceed 0,7 nanometers. Such structure may be formed from globules with very small sizes if densely packed. Therefore, synthesis of such silica gels is necessary to carry out under conditions which are favourable to formation of small globules, do not promote their growth and provide strong and uniform contraction of hydrogel at its transition in xerogel. The general and necessary conditions of synthesis microporous silica gels are the minimum rate of polycondensation reaction at all stages of silicon acid gel existence and the maximum value of capillary compression forces at drying. Thus for synthesis of silica gels with molecular-sieve properties the important factors are the minimum duration of processes of recondensation and constant dehydration rate. Proceeding from the above-stated, optimum conditions of formation of structure with molecular sieve properties are: pH of sol no more than 5, concentration of SiO_2 from 4,5 to 10 % mass, gel formation in a thin layer, washing out hydrogel from a reaction side product (sodium sulphate) at temperature no more than 323 K, constant speed of dehydration which is reached by drying in air flow.

On the basis of the revealed laws, silica gels with molecular-sieve properties are synthesised. They are characterised by specific surface area

$S_{sp} = 950 – 1000\ m^2/g$,

adsorption volume of pores

$V_s = 0,21 – 0,27\ cm^3/g$

and diameter of a pores

$d_p < 0,7$ nm,

and also their high dividing ability concerning hydrocarbons – components of natural gas is shown.

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