Physical Chemistry

I. B. SLINYAKOVA, G. B. BUDKEVICH, I. E. NEIMARK

1964

SovietRxiv

Abstract

Full Text

Physical Chemistry

I. B. SLINYAKOVA, G. B. BUDKEVICH, I. E. NEIMARK

HYDROPHOBIC HYDROGEN-SILICA ADSORBENT WITH AN Si–H BOND (HYDRIDE-POLYSILOXANE XEROGEL)

(Presented by Academician M. M. Dubinin, August 31, 1963)

Investigations carried out up to the present on the influence of the chemical nature of the surface of silica adsorbents on their adsorption properties have shown that, as a rule, chemical modification of the hydroxyl surface of silica gel leads to a sharp decrease in the magnitude of adsorption not only of polar substances, but also of nonpolar hydrocarbons (^{1}). Therefore such modified adsorbents are of practical importance only as fillers for polymeric materials, in gas-adsorption chromatography, and as nonswelling ion exchangers with a rigid skeleton. As adsorbents, modified silicas are of no interest, since chemical alteration of their surface leads to a decrease in the adsorption of various substances.

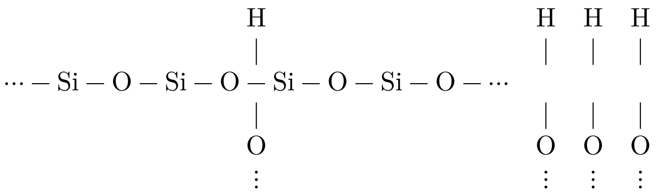
In accordance with present-day theoretical concepts, the reason for the decrease in the adsorption of modified adsorbents with respect to vapors of nonpolar substances is either the lower polarizability of the radical, as compared with the hydroxyl group, or the distancing of the adsorbed molecules from the surface layer of adsorption forces as a result of replacing hydroxyls by organic radicals of larger size (^{2}). Proceeding from these theoretical premises, we sought to obtain a silica gel on whose surface, instead of hydroxyl groups, there would be atoms incapable of forming hydrogen bonds, possessing high polarizability, and not exceeding the size of the hydroxyl group.

In the present communication we give the results of a study of the adsorption properties of the hydrogen-silica xerogel of hydridepolysiloxane synthesized by us, with an Si–H bond on the surface. This bond is very strong–the bond energy is 75 kcal; H^- has a high polarizability ($10.18 \cdot 10^{28}$ cm^3), and the covalent radius in hydrides is approximately equal to 0.3 Å (^{3}). “Hydrogen” silica gel was obtained by hydrolysis of an organosilicon compound, as a result of which a hydrogel of silanetriol, $(HSi(OH)_3)_n$, was formed; after drying it was a high-molecular porous substance of composition $(HSiO_{3/2})_n$. Analysis showed that the hydridepolysiloxane xerogel (“hydrogen” silica gel) contained 51.1% silicon. Hydrogen was determined in a Tserevitinov apparatus according to Kreshkov (^{4}). On treatment of the adsorbent with alkali, the amount of hydrogen evolved was 18.2 mmol per 1 g of adsorbent, or 1.82 wt.%, which is close to the theoretical value. Thus, the adsorbent obtained consists of a spatial siloxane network in

Fig. 1. Sorption isotherms of vapors of water (a), methyl alcohol (b), and hexane (c) on hydridopolysiloxane gel (1) and silica gel (2)

Figure 1: Fig. 1. Sorption isotherms of vapors of water (a), methyl alcohol (b), and hexane (c) on hydridopolysiloxane gel (1) and silica gel (2)

which each silicon contains hydrogen. The surface of the xerogel is uniformly covered with hydrogen atoms, which impart hydrophobic properties to it:



$$\begin{array}{ccccccccccccccccccc} & & & & & & & H & & & & & & & & H & H & H \\ & & & & & & & | & & & & & & & & | & | & | \\ \cdots - & Si & - & O & - & Si & - O - & Si & - & O & - & Si & - & O & - \cdots & & & \\ & & & & & & & | & & & & & & & & | & | & | \\ & & & & & & & O & & & & & & & & O & O & O \\ & & & & & & & \vdots & & & & & & & & \vdots & \vdots & \vdots \end{array}$$

Hydrogen silica gel is glassy and possesses sufficiently high strength; it does not dissolve in organic solvents. The xerogel is very hydrophobic; it can float on the surface of water in te-

for many months without wetting it. In the presence of saturated water vapor, it does not change its properties or composition. The hydrogen silica gel is stable up to 300°. To obtain the structural-sorption characteristics, sorption isotherms of vapors of water, methanol, and hexane at 20° were measured in a vacuum apparatus with quartz and spring balances. The low-temperature nitrogen sorption isotherm was determined in a volumetric vacuum apparatus.* Table 1 gives the structural-sorption characteristics of the hydrophobic xerogel of hydridopolysiloxane and, for comparison, of hydrophilic silica gel, whose porous structure approximately corresponds to that of the hydrogen silica gel.

Fig. 1. Sorption isotherms of vapors of water (*a*), methyl alcohol (*b*), and hexane (*c*) on hydridopolysiloxane gel (*1*) and silica gel (*2*).

In the xerogel of hydridopolysiloxane, the sorption pore volume with respect to hydrocarbons from their saturated vapors is 0.46–0.48 cm^3/g and is equal to the total pore volume. Consequently, macropores are absent in it. Characteristic of hydrogen silica gel is zero static adsorption activity from saturated water vapor over 20 days. Thus, hydrogen silica gel possesses great hydrophobicity and, at the same time, good organophilicity with respect to hydrocarbons ($V_s = 0.48\ cm^3/g$).

The adsorption properties of hydrogen silica gel were compared with those of hydrophilic silica gel having approximately the same specific surface area and pore radius. The predominant pore radius in the adsorbents under consideration, calculated from the differential curves of pore-volume distribution according to their effective radii (on the basis of the Kelvin formula), is the same and equals 14–15 Å. The specific surface area of hydrogen silica gel, calculated from hexane sorption isotherms and from the low-temperature nitrogen sorption isotherm by the BET equation, is, respectively, 507 m^2/g and 520 m^2/g. For hydrophilic silica gel this value is 518 m^2/g and was calculated from the methanol sorption isotherm. However, the silicic acid xerogel contains more transitional pores, which

* The nitrogen sorption isotherm was determined by N. P. Samchenko and A. I. Ponomarenko, to whom the authors express their gratitude.

was expressed in a larger value of the limiting sorption pore volume at $P/P_s = 1.0$ ($V_s = 0.56$—0.59 cm^3/g) (see Table 1 and Fig. 1).

When comparing, on hydrogen and hydrophilic silica gels, the sorption of different adsorbates at $P/P_s = 0.2$ (which approximately corresponds to monomolecular coverage), it is seen that if the amount of absorbed hexane vapors coincides, then the amount of adsorbed methanol vapors

Table 1

Structural-sorption characteristics of hydrophobic xerogel of hydridopolysiloxane and silica gel

Sample	True density, g/cm^3	Apparent density, g/cm^3	Total pore volume, cm^3/g	Adsorption at $P/P_s = 0.2$, mmol/g: H_2O	Adsorption at $P/P_s = 0.2$, mmol/g: CH_3OH	Adsorption at $P/P_s = 0.2$, mmol/g: C_6H_{14}	Sorption pore volume at $P/P_s = 1.0$, cm^3/g: H_2O	Sorption pore volume at $P/P_s = 1.0$, cm^3/g: CH_3OH	Sorption pore volume at $P/P_s = 1.0$, cm^3/g: C_6H_6	Sorption pore volume at $P/P_s = 1.0$, cm^3/g: C_6H_{14}	Specific surface area, m^2/g (BET): C_6H_{14}	Specific surface area, m^2/g (BET): N_2	H, wt. %
Xerogel of hydridopolysiloxane	1.60	0.93	0.46	0.04	1.90	1.40	0.00	0.48	0.46	0.47	507	520	1.82
Silica gel	2.20	–	–	4.00	4.00	1.40	0.59	0.57	0.59	0.57	518*	–	0.0

* The specific surface area was calculated by the BET equation from the methanol sorption isotherm.

on the xerogel of hydridopolysiloxane is 2 times smaller, and that of water is 100 times smaller, than on silica gel, whose surface is covered with hydroxyl groups (see Table 1). From Fig. 1, where the isotherms of sorption of water, methanol, and hexane vapors on hydrogen and hydrophilic silica gels are presented, it is seen that adsorption of the nonpolar hydrocarbon—hexane—on these adsorbents proceeds identically at small values of the relative pressure (the initial course of the isotherm curves coincides). The subsequent difference in adsorption of hexane is due to the different amount of transitional pores in these adsorbents.

Adsorption of water vapor on hydrophobic hydrogen silica gel practically does not occur over the entire range of relative pressures. Even at $P/P_s = 1.0$, no dense monolayer of water is formed on the surface of the xerogel of hydridopolysiloxane, which leads to the complete absence of capillary condensation. Methanol vapors are absorbed by hydrogen silica gel in a smaller amount than by hydrophilic silica gel. Consequently, the xerogel of hydridopolysiloxane, whose surface is covered with hydrogen atoms, is a specific adsorbent. The rather high adsorption of hexane, occurring due to dispersion forces, indicates that, evidently, the potential of the dispersion forces in hydrogen and hydrophilic silica gels is the same, irrespective of the chemical nature of their surface. The hydrogen layer of the xerogel of hydridopolysiloxane is not capable of forming donor-acceptor bonds; therefore water vapor is not adsorbed at all. In connection with the fact that hydrogen in the Si—H bond cannot form hydrogen bonds, adsorption of methanol on hydrogen silica gel is weak and is effected mainly only through dispersion forces.

Institute of Physical Chemistry named after L. V. Pisarzhevskii
Academy of Sciences of the Ukrainian SSR

Received
30 VII 1963

REFERENCES

1. I. E. Neimark, *Neftekhimiya*, **3**, 1, 149 (1963); I. B. Slinyakova, I. E. Neimark, *Koll. zhurn.*, **24**, 220 (1962).
2. M. M. Dubinin, *Izv. AN SSSR, OKhN*, 1960, No. 10, 1739; A. V. Kiselev, in: *Gas Chromatography*, Publishing House of the Academy of Sciences of the USSR, 1960, p. 45.
3. Ya. K. Syrkin, M. E. Dyatkina, *Chemical Bond and the Structure of Molecules*, 1946, pp. 228, 239, 309.
4. A. P. Kreshkov, V. A. Bork et al., *Analysis of Organosilicon Compounds*, Moscow, 1954, p. 183.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.