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THE ADSORPTION OF METHANOL VAPORS ON SILICA GEL Si-100 AND ITS SURFACE CONTAINING DIFFERENT CONCENTRATIONS OF CHEMICALLY BONDED FLUORIDE IONS

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Abstract

Synthesis of two types Si-100 silica gel with different concentrations of chemically bonded surface fluoride ions (2 and 4 μmol m^{-2}) was performed. Using gravimetric methods, adsorption isotherms of methanol as a function of its pressure in gas phase were measured for these adsorbents. It was found the strong surface deactivation of silica gel in relation to methanol with the increase of bonded fluoride ions concentration.

Keywords: adsorption, fluorinated surface, methanol vapors, silica gel

Introduction

Physical adsorption of vapors of chemical compounds for which the molecular dimensions are significantly smaller than mean pore radii occurs in a similar way as on flat surfaces [1, 2]. On the other hand, the number of moles of the compounds absorbed by mass unit of porous adsorbents depends either on mean pore diameter or on dimensions and geometrical structure of adsorbed molecules [3]. Subdivision of adsorbents [4–6] to adsorbents of elevated adsorption potential resulting from capillary effect is controversial, because the increase of adsorption potential depends not only on dimensions but also on geometrical structure of adsorbed molecules as well as on their susceptibility to the action of electrostatic field generated by the surface [7]. From this fact it results that the magnitude of interactions between adsorbent and adsorbate is very interesting in the respect of its utilization in chromatography and in the methods of adsorption separation or isolation of valuable components strongly dispersed in gas or liquid mixtures. Moreover, such optimization permits to utilize such adsorbents as collectors of gases and vapors of light hydrocarbons [6–8].

The aim of this work is the determination of the effect of hydrophobization degree of Si-100 silica gel surface on adsorption capacity of this gel in relation to methanol. Silica gel surface was hydrophobized by its dehydroxylation with fluoride ions. The adsorption ability of the initial Si-100 silica gel and its derivatives hydrophob-

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ized by fluoride ions in relation to methanol vapors was determined by gravimetric methods using vacuum apparatus consisted of quartz McBain balances. This apparatus was described elsewhere [9].

The weighed samples (0.5 g) of each adsorbent were placed in the columns of vacuum apparatus and after outgassing of the apparatus until the pressure of ca 10^{-3} millibars, the defined amounts of methanol vapors were introduced into the columns. After the establishment of adsorption equilibrium mass of adsorbed methanol was measured. The measurements were performed up to the values corresponding the adsorption at the pressure of saturated methanol vapor at room temperature.

Experimental

Materials and apparatus

Si-100 silica gel (Merck) of grain fraction of 0.12–0.20 mm and specific surface area of 343 $m^2 g^{-1}$ was used as adsorbent. Total pore volume V_p of this adsorbent was 0.7 $cm^3 g^{-1}$ and mean pore diameter determined from pore distribution curve plotted as $\partial V/\partial r$ *vs*. r was 109 *E*. Specific surface area S and pore volume V_p were measured on the basis of adsorption–desorption isotherms of nitrogen, assuming that the cross-section of nitrogen molecule is equal to 0.16 nm^2/molecule.

Preparation of adsorbents with chemically bonded fluoride ions

Before the synthesis, the isolated fractions of Si-100 silica gel were maintained for 24 h in the medium of saturated water vapor in order to complete surface hydroxylation. Then by the heating at 200°C for 8 h physically bonded water was removed from its surface. So prepared initial silica gel was subjected to the action of aqueous sodium fluoride solution of concentration permitting to obtain desirable concentration of bonded fluoride ions. Energy Si–F bond is 134 kcal mol^{-1} and is higher than energy of Si–C bond which is equal to 107 kcal mol^{-1} [10]. The number of fluoride ions bonded with surface area unit of silica gel (expressed in μmol m^{-2}) was determined titrimetrically on the basis of loss of these ions in the reaction solution. The adsorbent surface chemically modified with fluoride ions was washed several times with distilled water and then dried for 6 h at 200°C. In this way two types of adsorbents were prepared. These modified silicas contained on the surface 2 and 4 μmol m^{-2} of bonded fluoride ions (Si-100 F2 and Si-100 F4 respectively). Then by means of gravimetric method the adsorption of methanol vapors was measured both for adsorbents prepared in above-described method and for initial Si-100 silica gel. The results in the form of determined adsorption isotherms are presented in Figs 1–3.

Results and discussion

From Figs 1–3 it can be seen that the total adsorption including capillary condensation decreases significantly with the increase of the concentration of bonded fluoride

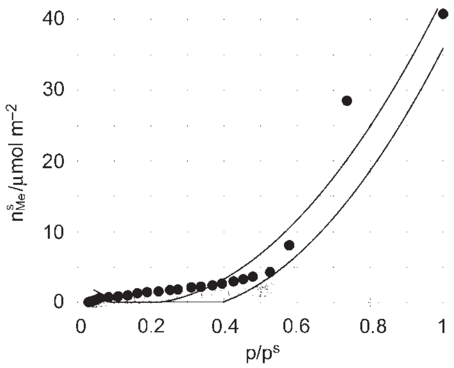

Fig. 1 Adsorption (light symbols) and desorption (dark symbols) isotherm for methanol vapor as a function of its relative pressure p/p^s on initial Si-100 silica gel surface

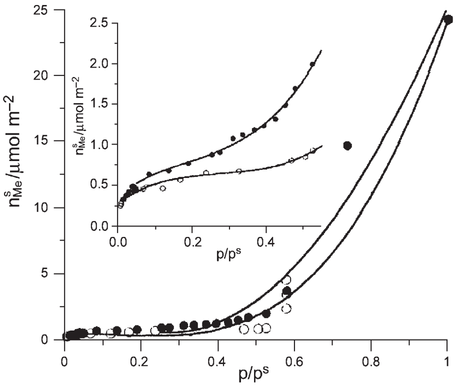

Fig. 2 Adsorption (light symbols) and desorption (dark symbols) isotherm for methanol vapor as a function of its relative pressure p/p^s on Si-100 F2 (silica gel surface modified with ions fluoride of 2 μmol m^{-2} concentration)

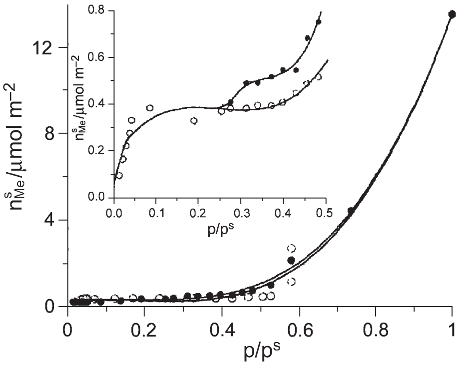

Fig. 3 Adsorption (light symbols) and desorption (dark symbols) isotherm for methanol vapor as a function of its relative pressure p/p^s on Si-100 F4 (silica gel surface modified with ions fluoride of 4 μmol m^{-2} concentration)

ions. The magnitude of the total amount of adsorbed methanol decreases from ca 42 µmol m^{-2} for initial Si-100 silica gel to 25 µmol m^{-2} for adsorbent containing 2 µmol m^{-2} of bonded fluoride ions (the decrease by 40.5%) and to 13.7 µmol m^{-2} for adsorbent containing 4 µmol m^{-2} of bonded fluoride ions (the decrease by ca 67.4%). Assuming that 1 m^2 of completely hydroxylated surface of Si-100 silica gel contains ca 8.5 µmol of OH groups, 2 µmol m^{-2} composes ca 23.5% and 4 µmol m^{-2} ca 47% of this total amount. In this connection it can be concluded that the elimination of 23.5% of surface OH groups causes the decrease of total adsorption by 40.5% and elimination of 47% of such groups reduces the magnitude of adsorption of methanol by 67.4%.

Initial sections of adsorption isotherms of methanol presented in these figures illustrate the decrease of the width of hysteresis loops with the increase of concentration of fluoride ions bonded with silica gel surface. The fact, that deactivation degree of initial Si-100 silica gel surface modified with fluoride ions is higher than this resulting from stoichiometric number of bonded ions may be explained by the ability of fluoride ions to the formation of the complexes with more than one OH group or by the blocking of the pores by high negative electrical charge [10].

Figure 4 illustrates the functional dependence of free adsorption enthalpy (ΔG) on the amount of methanol (expressed in J µmol^{-1} m^{-2}) adsorbed on initial and on chemically modified (with fluoride ions) silica gels. This thermodynamic function was calculated from equation [11, 12]: $-(\Delta G)_{T=\mathrm{const}}=2.303\,RT\log(p/p^s)$, where: R – gas constant, T – temperature (K), p – equilibrium pressure, p^s – pressure of saturated vapor over liquid methanol at temperature T. In this figure the sharp decrease of free adsorption enthalpy with the increase of coverage degree of the surface with methanol can be seen. This relates either to Si-100 silica gel (curve denote +) or to silica gels contained bonded fluoride ions of concentration of 2 µmol m^{-2} (curve o) and 4 µmol m^{-2} (curve ∆) after adsorption of about 0.5 µmol m^{-2} of methanol on Si-100 F4, 1 µmol m^{-2} of methanol on Si-100 F2 and 1.5 µmol m^{-2} on Si-100 (initial silica gel) the decrease of free enthalpy for low coverage of the surface with adsorbed methanol.

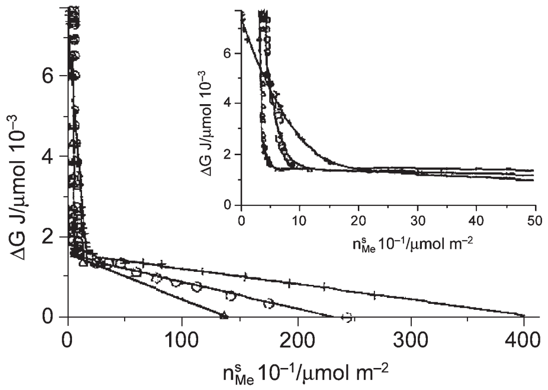

Fig. 4 Free molar enthalpy of adsorption of methanol vapor on initial silica gel Si-100(+); Si-100 F2 (o) and Si-100 F4 (∆) surface

The course of these curves shows that on starting silica gel the free enthalpy decreases most slowly whereas on silica gel of highest concentration of bonded fluoride ions (Si-100 F4) this enthalpy decreases most rapidly.

Dividing the maximum amounts of methanol absorbed by the surface area unit by maximum number of surface hydroxyl groups (8.5 μmol m^{-2}) it obtains the average number of molecules forming the adsorption layers on individual adsorbents. The average thickness of these layers is 5 times higher than the size of methanol molecule on starting silica gel, 2.8 times higher in the case of Si-100 F2 and 1.6 times higher in the case of Si-100 F4 silica gel.

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