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 \( \mu \)mol 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-
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 m² g⁻¹ was used as adsorbent. Total pore volume \( V_p \) of this adsorbent was 0.7 cm³ g⁻¹ and mean pore diameter determined from pore distribution curve plotted as \( \partial V/\partial r \) vs. \( r \) was 109 Å. 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 nm²/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