

Surface chemistry of silica and related sorbents

ADSORPTION OF POLYVINYLPIRROLIDONE AND POLYOXYETHYLENE WITH PURE AND MIXED SILICON, ALUMINIUM, AND TITANIUM OXIDES

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Abstract

Adsorption of polyvinylpyrrolidone (PVP) and polyoxyethylene (POE) from the aqueous solutions onto surfaces of individual and mixed silicon, titanium and aluminium oxides was studied. It was found that the values of polymer adsorption depend on composition of oxides. It was shown with IR spectroscopy that the surface of the oxides studied is fully accessible to interaction with PVP and POE.

Introduction

Water-soluble non-ionogenic polymers adsorb on fumed silica surfaces due to hydrogen bonds between electron-donating atoms of macromolecules and H atoms of silanol groups [1]. Heteroatoms (e.g., aluminium, titanium, etc.) in the silica structure cause the appearance of new active sites, which change the acid-base properties of the surfaces [2-6] and thereby can affect on polymer adsorption. The aim of this work was to investigate the influence of titania and alumina on the adsorption properties of mixed oxides based on highly disperse silica in respect to polyvinylpyrrolidone (PVP, average molecular weight 12000 determined viscosimetrically) and polyoxyethylene (POE, average molecular weight 600000). Such individual and mixed fumed oxides as silica A-100, A-175 and A-300; TiO₂; Al₂O₃, titania-silica TS-100; alumina-silicas AS-200 and AS-300 (Table) were studied by using adsorption and infrared (IR) spectroscopy methods.

Experimental

Polymer adsorption on the oxide surfaces was determined interferometrically from the difference in the polymer concentrations in the solution before contact with adsorbent and after ones for 24 h [7]. The measurement was carried out at the temperature 25±0.1°C. Mass of sorbent was equal to 500 mg, and the volume of polymer solutions was 50 ml. Adsorption value A was evaluated according to the formula:

$$A = (C - C_{eq}) V/m S_{BET}$$

where C and C_{eq} are the initial and equilibrium concentrations of the polymer respectively, V is the volume of the solution, m and S_{BET} denote the mass and specific surface area of adsorbent. The S_{BET} values of oxides differ significantly; therefore, the adsorption is shown in mg of polymer per 1 m² of the oxide surface.

The IR spectra of samples dried at room temperature were recorded using a Specord M80 (Karl Zeiss) spectrophotometer. For this purpose the samples were pressed into rectangular plates with the size of 5×22 mm and mass of 10 mg.

Results and discussion

The adsorption isotherms of polymers studied (Figs. 1-4) correspond to 2L (Langmuir type) for PVP or 3H (high affinity) type for POE, possessing significantly larger molecular weight compared to PVP, with different plateau adsorption. In the Langmuir equation coordinates $C_{eq}/A-C_{eq}$, the adsorption isotherms are direct lines. It has allowed to determine the maximal values of polymer adsorption A_{max} for samples studied (Table). As for the Langmuir theory, the value A_{max} corresponds to the capacity of a monolayer.

There is an inverse dependence of A_{max} on S_{BET} , which is in agreement with a reduction of the concentration of silanol groups with S_{BET} [8, 9], while such groups are the main adsorption sites for polar polymers, forming strong hydrogen bonds with these groups.

Table. Some characteristics of the studied oxides.

Oxide	S_{BET} , m ² /g	Oxide composition, wt.%			A_m , mg/m ²	
		SiO ₂	Al ₂ O ₃	TiO ₂	PVP	POE
A-100	100	100	-	-	1.00	0.93
A-175	175	100	-	-	0.85	
A-300	287	100	-	-	0.68	0.65
Al ₂ O ₃	140	-	100	-	0.15	0.10
AS-200	197	98	2	-	0.49	0.42
AS-300	319	89	11	-	0.50	0.27
TiO ₂	23	-	-	100	0.73	0.50
TS-100	108	79	-	21	0.50	0.70

After introduction of titanium and aluminium oxides into a silica matrix different aprotic acid sites also appear on a surface besides hydroxyl groups [3-5]. Therefore it would be hypothetically possible to expect the higher sorption activity for the mixed oxides in relation to polymers, than that in case of individual SiO₂. However really the values of the maximum adsorption of polymers studied on titania- and alumina-silicas appeared to be lesser, than those on initial silica (Table, samples A-100 and TS-100, A-175 and AS-200, A-300 and AS-300).

Primary particles of studied mixed oxides consist of separate phase grains of silica and oxides of titanium or aluminium paired with titanosiloxane or almosiloxane bonds [10-13]. The surface of such oxides also contains silica, titania- and alumina patches. To define their role in researched processes, the isotherms of adsorption of polymers on the surface of individual oxides of titanium and aluminium were obtained. The value of PVP and POE adsorption appeared to be diminished in the series of SiO₂ > TiO₂ > Al₂O₃. It is possible to assume that it is caused by decreasing proton-donating properties of free surface OH-groups of the specified oxides, this being testified by the shift of absorption bands of free hydroxyl

groups, in particular, at adsorption of diethyl ether, which amounted for SiO₂ - 460, TiO₂ - 306, and Al₂O₃ - 270 cm⁻¹ [14]. It is possible to conclude from given that no interaction between electron-donating oxygen atoms of PVP or POE and surface Lewis sites occurs, and the adsorption of polymers is caused extremely by formation of hydrogen bonds with free hydroxyl groups. The replacement of silica surfaces by titania or alumina results in overall decrease of polymer adsorption.

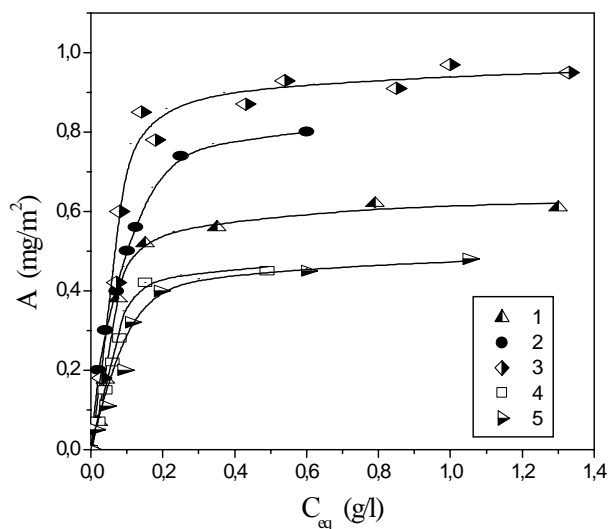


Fig. 1. Adsorption isotherms of PVP on silicas A-300 (1), A-175 (2), A-100 (3) and alumina-silicas AS-200 (4), AS-300 (5).

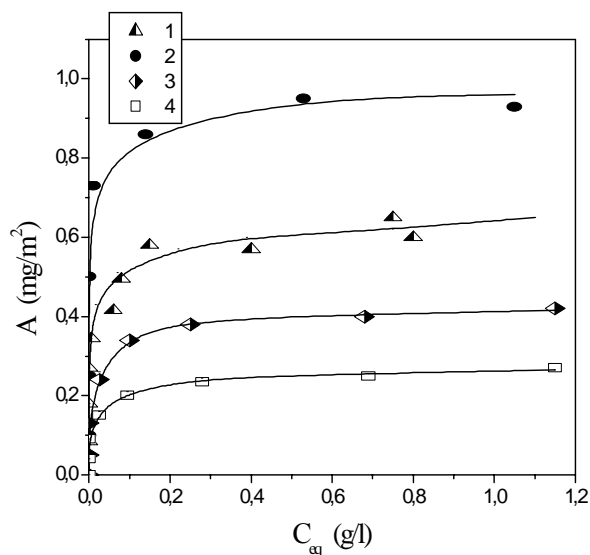


Fig. 2. Adsorption isotherms of POE on silicas A-300 (1), A-100 (2), and alumina-silicas AS-200 (3), AS-300 (4).

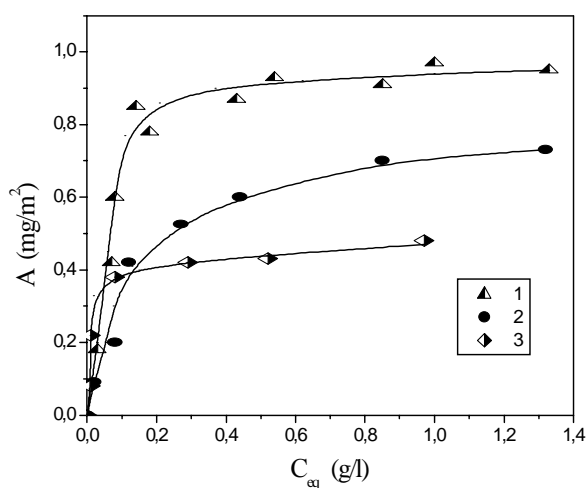


Fig. 3. Adsorption isotherms of PVP on silica A-100 (1), TiO₂ (2), and titania-silica TS-100 (3).

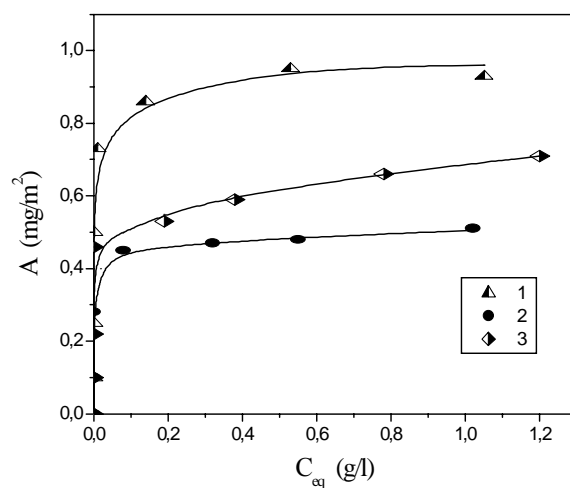


Fig. 4. Adsorption isotherms of POE on silica A-100 (1), TiO₂ (2), and titania-silica TS-100 (3).

In the IR spectra of individual silica and mixed oxides, there is an intensive narrow band of free silanol groups with a maximum at 3750 cm^{-1} (Fig. 5, curve 1).

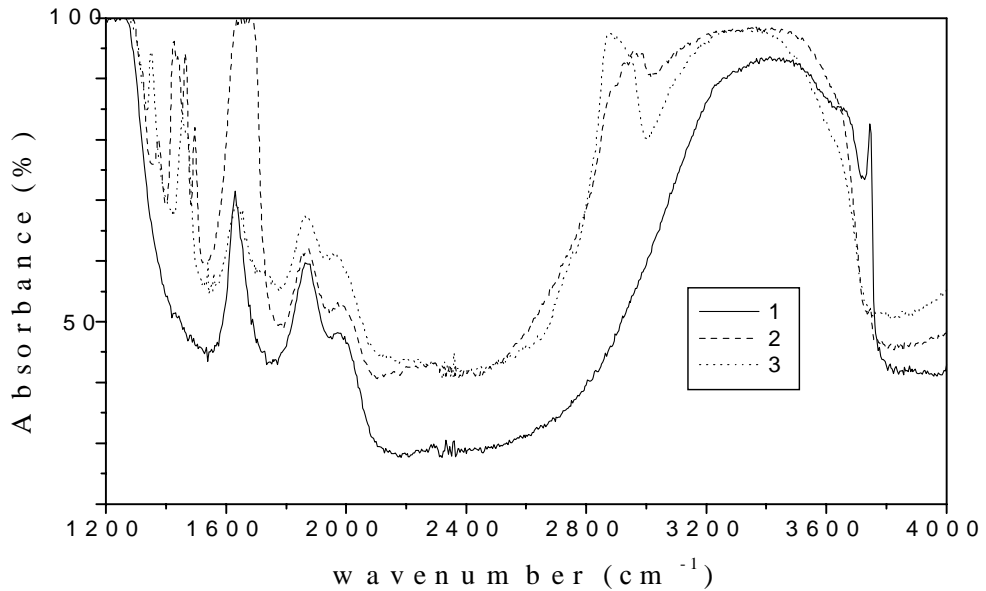


Fig. 5. IR spectra of silica A-300 after contact with liquid water (1) and solution of PVP (2) and POE (3).

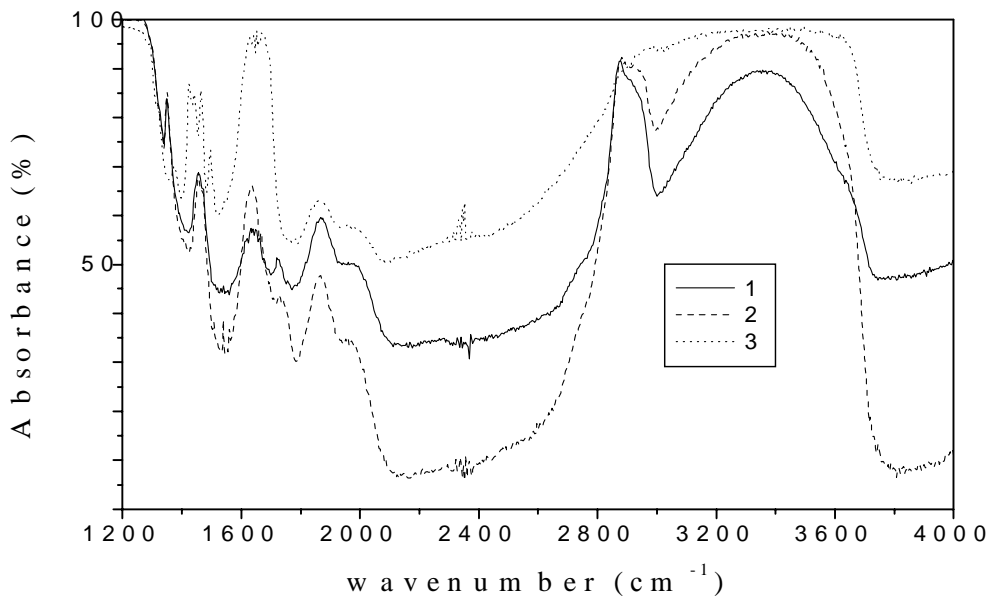


Fig. 6. IR spectra of samples A-100 (1) and AS-200 (2) after adsorption of POE and of sample TS 100 after adsorption of PVP (3).

Absorption bands, which could be interpreted as IR-spectral display of surface Ti-OH or Al-OH groups are not observed. The reasons of this effect are not clear now. It is supposed [10] that they can be masked by bulk absorption of the various forms of sorbed water. During adsorption of polymers the intensity of the band at 3750 cm^{-1} reduces and a broad band of the disturbed OH-groups with a maximum at 3348 cm^{-1} appears (Fig. 5, curve 2). It is fixed that for all silica containing samples as adsorption reaches the value A_{\max} the band at 3750 cm^{-1} disappears completely (Figs. 5, 6), i.e. all silanol groups on the surface of studied oxides interact with polymers. In the literature [11, 15] it is supposed that one of the reasons of rising of the acidity of mixed oxides based on silicon dioxide is the polarisation of silanol groups owing to inductive effect caused by the presence of heteroatoms. The fact, the wavenumber of silanol groups at 3750 cm^{-1} and a value of displacement under adsorption of polymers $\sim 400\text{ cm}^{-1}$ for all the samples are the same that testifies an invariance of $\equiv\text{Si-OH}$ groups acidity. Differences in chemical and catalytic properties of individual silica and mixed oxides on its basis [2, 5, 15] are caused, apparently, by the surface heteroatoms forming new active sites.

Conclusion

Thus, the IR spectra testify that the investigated adsorptive processes proceed immediately on the surface of primary particles of pyrogenic oxides, accessible not only for interaction with rather small molecules of silanes [1, 5], but also with voluminous macromolecules of polymers. Thus, the main mechanism of adsorption PVP and POE is the formation of hydrogen bonds between electron-donating atoms of polymers and H atoms of hydroxyl groups of the oxide surface even with the presence of others not only hydroxyl active sites.

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