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Investigation of the Porosity of Silica and Alumina with Chemically Bonded Polystyrene

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Abstract. The effect of modification of porous silica and alumina with a copolymer of styrene and vinylsilane on the porosity of oxides have been investigated by means of low temperature nitrogen sorption. Only small changes of the specific surface area and of the specific pore volume were observed on modification of oxides with non-cross-linked copolymer. The specific surface area significantly increased after the cross-linking of the deposited polymeric layer while the specific pore volume remains almost unaffected. A broad hysteresis loop appears in the nitrogen sorption isotherm for the alumina modified with the cross-linked polymer. The porosity of oxides modified by chemisorption method differed strongly from that observed for composites modified by physisorption of polymer.

Keywords: silica, alumina, composite, nitrogen sorption, porosity

Introduction

Over last decade considerable attention has been paid to materials composed of rigid inorganic porous supports and organic polymers. Such composites show a significant improvement of mechanical properties over pure polymers. Silicas and aluminas were mostly employed as inorganic supports. The roughness of oxide particles was recognized as an important parameter for giving sufficient adhesion between the polymer and the oxide. Thus, a number of studies discuss the adhesion phenomena in context with the fractal dimensions of the polymers and the oxides (Douglas, 1989; and references therein). Little attention, however, has been paid to the changes of the porosity of oxides after the modification with polymers. When depositing a polymer on a porous oxide the amount can be increased to such a level that the pores of the support are totally filled. However, most investigations deal with composites where the polymer content is much less than is required for the total filling of pores. In fact, a high content of polymer in composites results in an annihilation of porosity by filling and/or closing the pores with polymer.

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The porosity of composites with low polymer content was more intensively investigated in the field of adsorption, because the use of these materials as adsorbents promises interesting adsorption properties and increased chemical stability over conventional packings. These materials have been preferably applied as adsorbents in analytical and preparative separation processes (Figge et al., 1986; Kurganov et al., 1990; Hanson et al., 1993; Ivanov et al., 1992). The desirable structure of a composite adsorbent is a thin polymeric film closely and densely bonded onto the inner and outer surface of the porous support. The porosity of support should not be significantly changed during the preparation of composite. Accounting for these requirements, the main investigations of the porosity of composites were concerned with the determination of the specific surface area, which should still remain available for the adsorption. Recently, more detailed investigations on the porosity of composite adsorbents were performed by Hanson et al. (1993) and Neimark et al. (1993), who studied the changes of porosity of chromatographic grade silicas on the modification with physisorbed polymers. Preservation of the pore size distribution and of the mean pore diameter was observed, in spite of a strong decrease of the specific surface area and the specific pore volume with an increase of the polymer mass load. A model of the specific pore filling with the polymer was suggested to explain the phenomenon.

In this work we report on the results of an investigation of the porosity of composite materials prepared by means of chemisorption of polymers onto the surface of chromatographic grade silicas and one alumina. The deposition of the polymer onto the oxidic surface, its modification and cross-linking have been performed in separate steps, which allows one to investigate the effect of the formation of the polymeric network on the total porosity of the composite. The changes observed are compared with the porosity of composites prepared by physisorption deposition.

Experimental

Chemicals and Materials

Chromatographic grade silicas: LiChrospher Si 300 (two samples) and LiChrospher Si 100 and chromatographic grade alumina Aluspher 100 were obtained from Merck, Darmstadt, Germany. A silica with mean pore diameter of 50 nm was obtained as a gift from MZ Analysentechnik, Mainz, Germany.

All solvents employed for the surface modification were of analytical reagent grade and were used without additional purification.

Synthesis of copolymer of styrene and vinylmethyldiethoxysilane (CSVS) was performed as described elsewhere (Kurganov et al., 1994). The mean molecular mass of copolymer was calculated to 5,500 Daltons using Size-Exclusion Chromatography (SEC) with polystyrene standards supplied by Polymer Service, Mainz, Germany. The ratio of styrene to silane in the copolymer was found to be 8:1 based on elemental analysis.

Synthesis of Polymer Bonded Oxides

Coating of the Oxides with a Copolymer of Styrene and Vinylmethyldiethoxysilane (CSVS). A weighed amount of silica or alumina was placed in a three-necked flask equipped with a stirrer and Dean-Stark separator and 100 ml of toluene per 10 g of oxide were added. The suspension was heated under reflux until no water was liberated. Then a solution of CSVS in toluene was added (ca. 0.2 mg of CSVS per square meter of specific surface area of support). The suspension was heated under reflux for 5 hrs. The hot suspension was filtered off, washed twice with hot toluene and dried under vacuum at 60°C. The amount of bounded CSVS was assessed by means of elemental analysis (Table 1).

Chloromethylation of Immobilized CSVS. The chloromethylation of immobilized CSVS was performed according to the conventional procedure (Kurganov et al., 1994) by reaction of the composite with a mixture of thionyl chloride, dimethoxymethane and zinc chloride in dichloroethane at room temperature during 48 hrs. The suspension was filtered off and washed with dichloroethane. The degree of chloromethylation ranged between 85–95% was determined by means of elemental analysis.

Cross-Linking of the Chloromethylated CSVS. Cross-linking of the chloromethylated CSVS was carried out by boiling a suspension of chloromethylated composite in dichloroethane or toluene in the presence of zinc chloride as a catalyst. With dichloroethane as a solvent cross-linking occurred, whereas in toluene the cross-linking was additionally accompanied by an arylation of polymer with toluene. In the latter case

Table 1. Characteristic parameters of native oxides and modified materials with non-cross-linked and cross-linked polymeric layers: m = mass polymer content (mg/g), a_s = specific surface area according to BET (m^2/g), V_p = specific pore volume according to Gurvich (ml/g), d_p = mean pore diameter (nm) and C = parameter of BET equation, S = specific surface area of cross-linked polymeric layer (S).

		Values per g of material					Values per g of oxide			
Material	Type of modification	m mg/g	a_s m^2/g	V_p cm^3/g	d_p nm	C	m mg/g	a_s m^2/g	V_p cm^3/g	S^3 m^2/g
Cross-linked polystyrene	none	–	715	0,22	1,8	138	–	–	–	715
Aluspher 100	none	–	154	0,502	130	122	–	154	0,502	
	PS-coated	43	140	0,427	121	81	45	146	0,446	
	cross-linked	61	175	0,435	99	71	65	186	0,463	492
Aluspher 100	none	–	155	0,5	129	130	–	155	0,5	
	PS-coated	46	138	0,44	127	60	48	144	0,459	
	cross-linked	54	184	0,463	100	115	57	194	0,489	877
LiChrospher Si 100	none	–	352	1,231	140	149	–	352	1,231	
	PS-coated	96	282	0,954	135	32	106	312	1,055	
	cross-linked	137	370	1,02	110	53	158	429	1,182	487
LiChrospher Si 300	none	–	59	0,56	384	264	–	59	0,56	
	PS-coated	74	64	0,52	319	46	82	69	0,56	
	cross-linked	77	123	0,58	189	89	83	133	0,63	891
LiChrospher Si 300	none	–	78	0,68	341	175	–	78	0,68	
	PS-coated	88	79	0,61	308	55	96	87	0,67	
	cross-linked[1]	100	173	0,59	137	85	111	192	0,65	1027
	cross-linked[2]	134	159	0,56	141	77	154	184	0,65	1377
Silica 50 nm	none	–	58	0,67	462	307	–	58	0,67	
	PS-coated	54	59	0,61	414	36	57	61	0,64	
	cross-linked	52	96	0,62	258	70	55	101	0,65	782

[1] Cross-linked in dichloroethane, see Experimental.

[2] Cross-linked in toluene, see Experimental.

[3] $S = (a_S^{\text{composite}} - a_S^{\text{oxide}})/m$, where $a_S^{\text{composite}}$ is the specific surface area of composite per g of oxide, a_S^{oxide} is the specific surface area of oxide, m is the polymer content of composite per g of oxide.

the degree of cross-linking was lower, but the resulting carbon content was higher as compared with the cross-linking in dichloroethane. The completeness of cross-linking was monitored by means of elemental analysis of the product.

Low-Temperature Nitrogen Sorption

The nitrogen sorption isotherms of original oxides and of composites were measured at 77 K with an ASAP 2400 system (Micromeritics, Norcross, CA, USA) and with the Omnisorp (Coulter Counters, USA). The specific surface area according to BET, the specific pore volume according to Gurvich and the pore size distribution according to BJH method were calculated from the nitrogen isotherms by means of the standard software implemented in the ASAP 2400 system or with Milestone Advanced Data Processing implemented in the Omnisorp system. The micropore volume was calculated using the t-plot derived from the nitrogen sorption isotherm.

Results and Discussion

The pore structure characteristics of the porous oxides, the polymer and the synthesized composites are collected in Table 1. Columns 3–7 of Table 1 contain the directly recorded characteristics of composites, i.e., per 1 g of material. Two main features can be noted in the table: a strong decrease of the parameter C of polymer coated materials as compared with the original oxides and a remarkable increase of the specific surface area of composites after cross-linking of the immobilized polymeric layer.

A decrease in the value of C is usually observed on the modification of oxidic surface with adsorbate (Parfitt et al., 1975) or with chemical reagents, i.e., silanes (Kiselev, 1961), and commonly explained by a transformation of the high adsorption energy surface of the oxide into a low energy adsorption surface after modification (Bain et al., 1989). For the purpose of this work a decrease in the value of C can be regarded as an indication that the copolymer has significantly modified the surface of oxides.

An increase of the specific surface area was observed for all cross-linked composites and in this respect the chemisorption method of modification differs strongly from physisorption where a strong decrease of the specific surface area was observed (Hanson et al., 1993). In the initial stage of modification when a non-crosslinked polymer was deposited onto the surface of porous oxide, the change in the specific surface area of the modified support was small (Table 1). To make a comparison with the parent oxides more reliable the experimental values have been recalculated per 1 g of oxide in the composite. The data obtained are presented in columns 8–10 of Table 1. One can see, that the specific surface area of oxides of a mean pore diameter of 10 nm decreased by 5–10% after depositing the polymer, while it increased in the case of wide-pore silicas to approximately the same extent. A decrease in porosity of the small-pore oxides can be explained by blocking fine pores with deposited polymer, because it is well-known, that gel-type polymers provide no porosity in a dry state (Freeman and Poinescu, 1977). Blocking of small pores should be less significant for wide-pore silicas. The increase of the specific surface area is probably a result of a contribution of the outer surface of polymeric coils immobilized onto the silica surface.

The specific surface area of composites with cross-linked polymeric layer exceeds the specific surface of parent oxides by 25–100% (Table 1). Simultaneously, the specific pore volume of the composites differs by 10% or lower from the specific pore volume of parent oxides. This difference is even smaller for composites with cross-linked polymeric layer than for non-cross-linked composites (Table 1). A possible explanation is that either the polymer modification took place at the outer surface of particles while the inner surface of pores remained unaffected, or a highly porous thin polymeric layer was formed on both the inner and outer surface. Accounting for the synthetic procedure applied and for a strong decrease of the coefficient C on modification the first assumption can be neglected. The scanning electron micrographs of the modified LiChrospher Si 300 did not show either any polymer agglomerates on the outer surface of particles or in the interparticle space. Therefore, the formation of a highly porous polymeric layer is highly probable. Its specific surface area can be calculated by division of the difference between the specific surface areas of parent (column 9, Table 1) and modified (column 4, Table 1) silica by the amount of polymer deposited (column 8, Table 1). The calculated values (S, last column in Table 1) range in between 500 and 1000 m^2 per g of polymer. They coincide fairly well with the specific surface area of the pure polymer synthesized by the same method (Davankov and Tsurupa, 1990). Variations of the calculated values can be explained by different degree of cross-linking of polymeric layer achieved for samples in the synthesis. The higher degree of cross-linking, the higher the specific surface area of the polymeric layer is observed (Davankov and Tsurupa, 1990). Besides, the accuracy of calculations is strongly affected by the measured difference in the specific surface areas of composite and its native oxide.

It should be emphasized, that formation of the porous polymeric layer is the result of a special cross-linking procedure, which leads to the formation of a network of quite different structure than is commonly observed for cross-linked gel type polymers (Davankov and Tsurupa, 1990). The porosity of this type of polymer appears when a high degree of cross-linking is obtained from the polymer in swollen state. Therefore, dichloroethane and toluene, which are both good solvents for polystyrene, have been used in the synthesis. In dichloroethane the cross-linking degree is expected to be higher than in toluene where the cross-linking was accompanied by the arylation of polymer. Therefore, some chloromethyl groups were excluded from the cross-linking reaction. Nevertheless, no significant difference in the porosity of composites synthesized in these two solvents was observed, although the polymer content of composite synthesized in toluene was higher (Table 1). Hence, one can conclude that extent of cross-linking even for the composite synthesized in toluene was high enough because the remarkable porosity of this type of polymer was observed for a cross-linking degree of ca. 50% or higher (Davankov and Tsurupa, 1990).

High values of the specific surface area of the polymeric layer calculated above indicate the existence of small pores (micropores) in the polymeric film. In Fig. 1

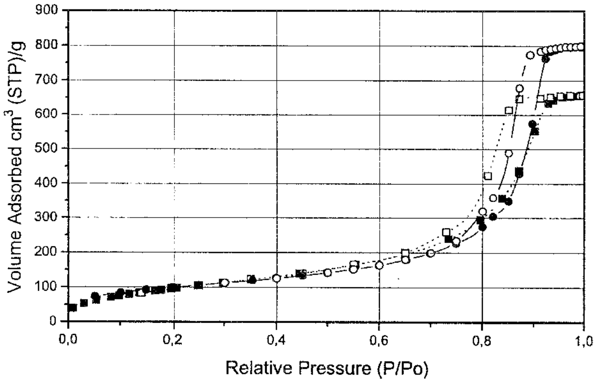

Figure 1. Nitrogen sorption isotherms at 77 K on the silica LiChrospher Si 100 (○) and on its composite with the cross-linked polymeric layer (□). Closed symbol-adsorption, open symbol-desorption.

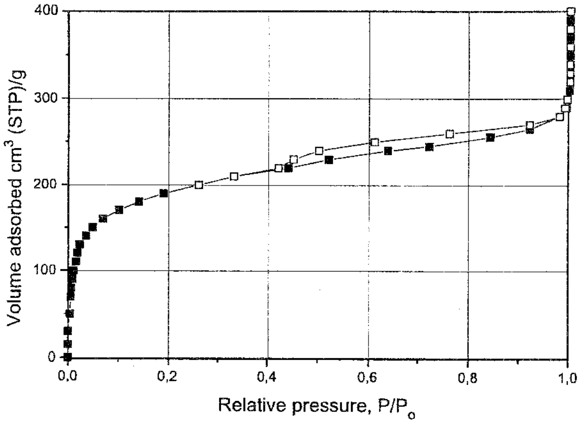

Figure 2. Nitrogen sorption isotherm on Styrosorb (cross-linked polystyrene).

the adsorption isotherms of LiChrospher Si 100 and its composites are shown as a typical example. The adsorption and desorption isotherms of silica and its composites look very similar. Inspection of the isotherms and t-plot analysis reveals that no significant microporosity has developed as a result of the cross-linking of immobilized polystyrene.

In contrast to the cross-linked composite, the sorption isotherm of the cross-linked pure polymer (Fig. 2) shows a much greater uptake of nitrogen at low relative pressure. The isotherm is essentially of Type I and the calculated mean pore diameter is of about 2 nm (Fig. 3). This value is on the border line between the micropores and mesopores. Only a small hysteresis loop was observed for the cross-linked polymer. Comparing the adsorption isotherm of cross-linked polymer with that of the silica composite having the cross-linked polymeric layer, one can see that they have different porosities. Instead of a relatively narrow pore size distribution with a mean pore diameter of ca. 2 nm, the polymeric layer in the composite possesses a broad pore size distribution in the range of 2 to 10 nm (Fig. 4).

The sorption isotherm of the alumina based composite reveals another phenomenon, which was not observed for the silica based materials. The alumina based composite displayed an extremely large hysteresis loop (Fig. 5). Its adsorption isotherm looks very similar to that of the non-modified oxide as was also observed for the silica based composites. Large differences exist in the desorption branches of isotherms, where the step corresponding capillary evaporation was shifted to much lower p/p_0 for the composite based on alumina. As a result a large hysteresis loop exists in the

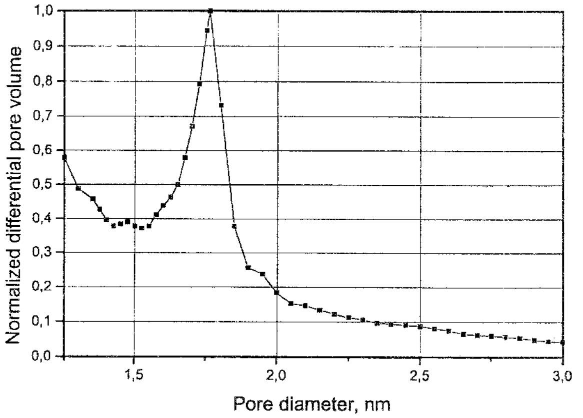

Figure 3. Pore size distribution of Styrosorb from the desorption isotherm.

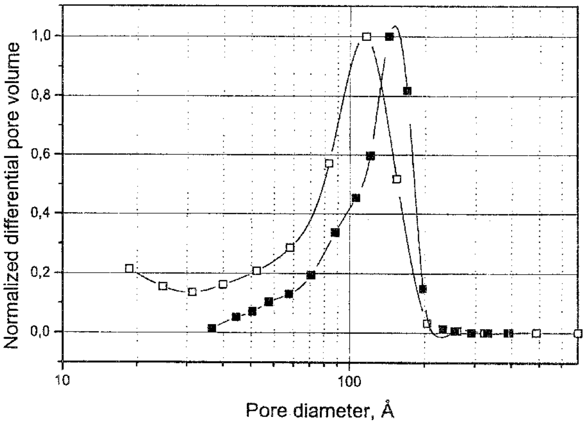

Figure 4. Pore-size distribution of the silica LiChrospher Si 100 (■) and its composite with the cross-linked polymeric layer (□) from the desorption isotherm.

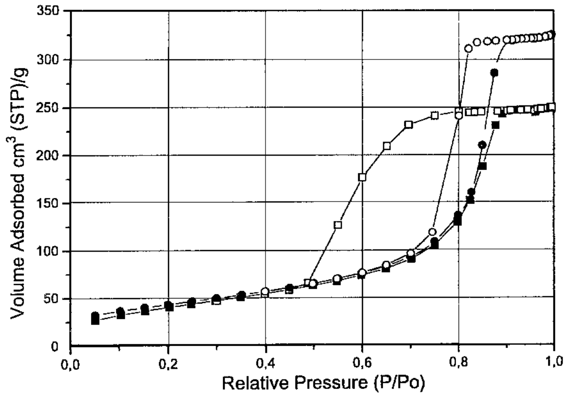

Figure 5. Nitrogen sorption isotherm on the alumina Aluspher 100 (■) and on its composite with the cross-linked polymeric layer (○). Closed symbol-adsorption, open symbol-desorption.

sorption isotherm. Again, no microporosity could be derived for this composite from the measured adsorption isotherms and the increased hysteresis is probably due to contraction of the pore opening during the cross-linking of the polymeric layer.

Conclusions

The effect of the modification of porous silicas and aluminas by means of chemisorption of copolymer of styrene and vinylsilane on the porosity of oxides has been investigated. Only small changes of the specific surface areas and the specific pore volume have been observed on the first stage of synthesis, when the copolymer was deposited onto the surface. The subsequent cross-linking of the deposited polymeric layer significantly increased the specific surface area of the composite and decreased the mean pore diameter while the specific pore volume was only slightly changed after cross-linking. The highly developed porosity of the cross-linked polymeric layer appears to be due to the small pores of broad size distribution in the range between 2 and 10 nm, while no microporosity of polymeric layer could be found from the *t*-plot analysis.

The porosity of oxides modified by the chemisorption method differed strongly from that observed for the composites modified by physisorption of polymers (Neimark et al., 1993). The main feature of the latter type of modification is a strong decrease of the specific surface area and the specific pore volume with an increase of polymer mass-loading, while the mean pore diameter and even the pore size distribution remained unaffected. Therefore, the two methods of the modification produce composites with different structures of the polymeric layer.

Another interesting aspect of this work is that the chemical nature of the oxide appears to influence strongly the pore structure of the polymeric layer formed on its surface. The cross-linked polymer formed in the adsorbed state provides a broad pore size distribution shifted to higher pore sizes than its counterpart formed in a solution. The polymer on the surface of alumina produces a greater change in the pore structure (probably by decreasing the size of the pore entrances) than was observed for the silica based composites. As a result a broad hysteresis loop appears in the nitrogen isotherm for the alumina modified with the cross-linked polymer.

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