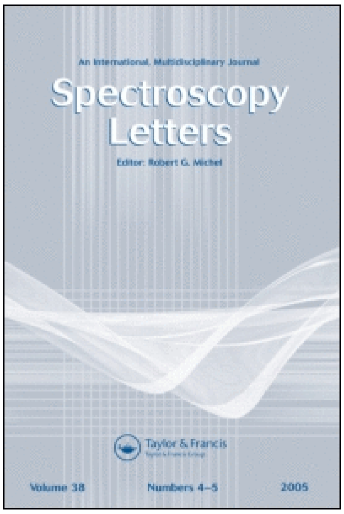

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Infra Red Investigations of Different Kinds of Synthetic Active Silicas

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INFRA RED INVESTIGATIONS OF DIFFERENT KINDS OF SYNTHETIC ACTIVE SILICAS

KEY WORDS: Active silicas, infra red spectra,
structure investigations

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INTRODUCTION

The results of investigations of active silicas do not permit an unambiguous description of their structure, which is different for each kind of this material. Aerogels, xerogels or the so called precipitated silicas have different physical properties, due to the application of empirically established conditions of precipitation or condensation of polysilicic acids.

Silicas of high specific surface area are known to be amorphous. Nevertheless there are suggestions, that their surface structure is more or less ordered1), 2), 3). Snyder and Ward[3)] investigated the properties of active silicas on a series of samples, which differed widely in surface area and pore diameter. The authors suggested, that the surface properties of such silicas depend on the degree of surface regularity or crystallinity. Factors, which promote the 'crystallinity' of silicas during their synthesis will favour large crystallite size and increased pore diameter.

Investigations were started, to find some relations between the physicochemical properties, obtained by conventional methods, such as the apparent and compacted bulk density, the water and mineral oil adsorptive capacity, the specific surface area and average pore diameter and the absorption properties in the infra red of silica samples.

The results of the i.r. measurements confirm the conclusions of Snyder and Ward, concerning the different regularities of structure and their relation to the pore diameter size of active silicas. The different kinds of silicas, such as precipitated white rubber fillers, Aerosils, fine and large pore silica gels and the beer stabilizer Piwator, show some differences in their i.r. spectra, which in some cases allow to distinguish the specific kind of silica.

EXPERIMENTAL

Samples

1. Ultrasil VN3(I) and VN3(II) - white rubber fillers from Chem. Fabrik Wesseling, Degussa, West Germany;

2. Arsil I, Arsil II, Arsil III - white rubber fillers prepared in the laboratory by precipitation from sodium silicate solution with sulphuric acid solution at pH 4-4,5 at 80°C[4];
3. Arsil IV - white rubber filler obtained in the industrial process, basing on the precipitation from sodium silicate solution with sulphuric acid solution[4];
4. Aerosil from Degussa, West Germany;
5. Large and fine pore silicagels from Inowrocławskie Zakłady Chemiczne, Poland;
6. Piwator - xerogel for beer stabilization, obtained in the laboratory by precipitation from sulphuric acid solution with sodium silicate solution at pH 6-7 at room temperature[5].

The i.r. spectra in the range of 400-4000 cm^{-1} were measured with the C.Zeiss Jena UR-10 spectrophotometer. The samples dried at 110°C were pelleted with KBr. The vibration band 1110 cm^{-1} was chosen to demonstrate the variations of the band sharpness among the spectra of different kinds of silicas (Fig. 1). The 1110 cm^{-1} bands shown on Fig.1 were registered as absorbancy vs. ware number, using the UR-10 "Zweitschreiber" detachment, to enable the measurement of the apparent band intensities either as absorption difference at 1110 cm^{-1} or as band area by the base line technique. The results are presented in Tab.1, where also the values of apparent and compacted bulk densities, of water and mineral oil adsorptive capacities, of specific BET surface areas, and of average pore diameters are

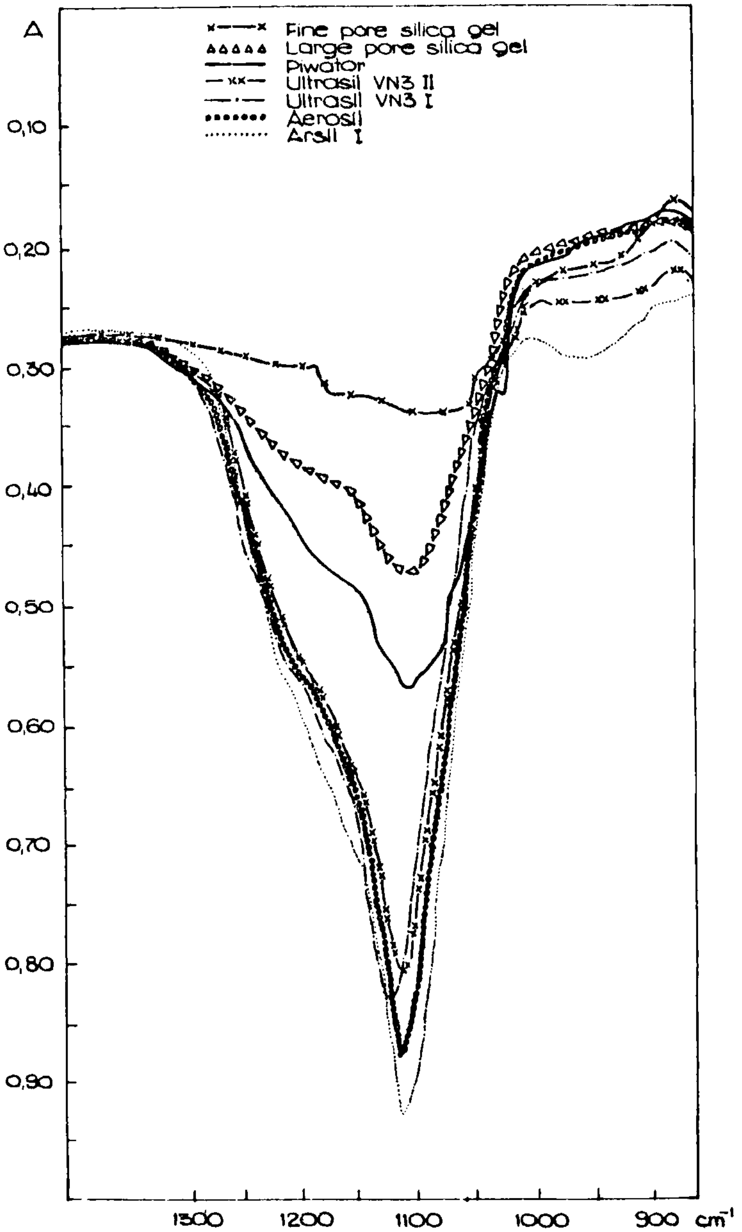

Fig. 1. The i.r. spectra of different kinds of active silicas in the range of 900-1400 cm^{-1} (0,125% of samples dried at 110°C in 0,4g KBr pellets)

Table 1

Physico-chemical properties of active silicas

Kind of active silica	Apparent bulk density kg/m^3	Compacted bulk density kg/m^3	Water adsorptive capacity g/100 g	Mineral oil adsorptive capacity g/100 g	SpecificBET surface area m^2/g	1110 cm^{-1} band area dm^2	1110 cm^{-1} band height ΔA	Average pore diameter $\bar{d}$, Å
Aerosil	80	136	312	275	355	0,300	0,608	58,6
Ultrasil VN3/I/	88	186	225	183	216	0,325	0,588	60,7
Ultrasil VN3/II/	94	235	190	185	231	0,306	0,557	-
Arsil I	50	143	190	205	328	0,335	0,656	-
Arsil II	93	207	190	220	200	-	-	53,2
Arsil III	86	226	230	229	173	-	-	59,0
Arsil IV	92	236	215	204	-	0,335	0,628	-
Large pore silica gel	165	433	160	133	420	0,162	0,252	-
Fine pore silica gel	314	682	105	79	428	0,075	0,110	-
Piwator	160	425	135	149	445	0,210	0,338	-

given. The spectra on Fig. 2 and 3 allow one to observe after calcination of samples at different temperatures the decrease of the intensity of the 960 cm^{-1} absorption band characteristic for the precipitated white rubber fillers, such as Arsil I and Ultrasil. The spectra of Aerosils and large pore silica gels showed no absorption in the range of 960 cm^{-1}. In case of the beer stabilizer Piwator the 960 cm^{-1} absorption band appeared as a broad shoulder on the 1110 cm^{-1} band. Similar not well defined 960 cm^{-1} bands were observed in case of fine pore silica gels.

For samples mostly differing in the intensity of i.r. spectra, such as Ultrasil and Arsil on one hand and fine pore silica gel on the other, X-ray diffraction measurements were

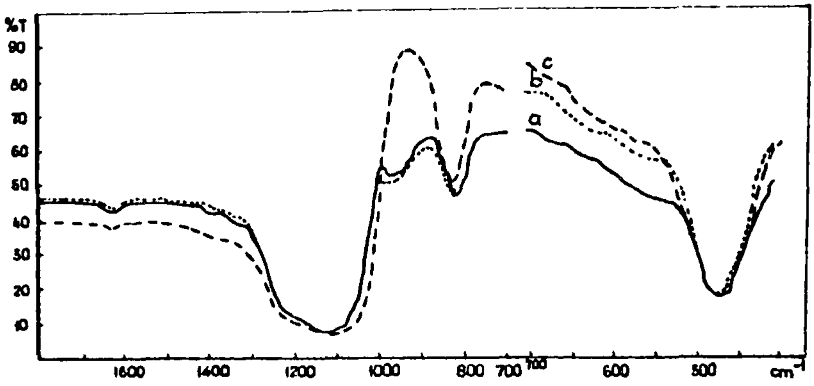

FIG.2. I.r. spectra of Ultrasil VN3 (I) (0,25% in 0,8 g KBr pellets), a) before drying, b) after drying at 140°C, c) after calcination at 600°C.

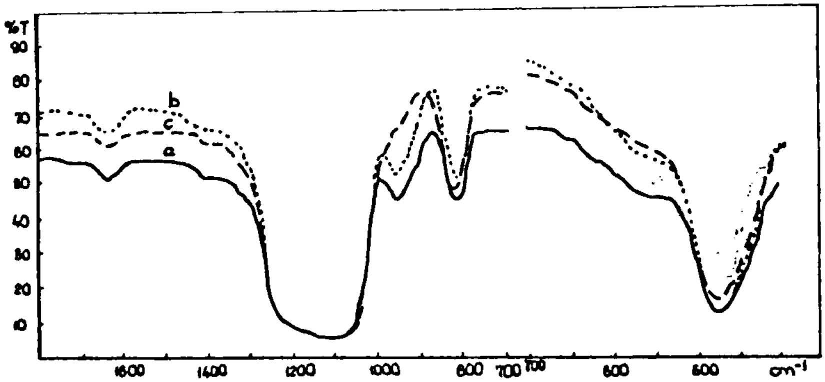

FIG.3. I.r. spectra of Arsil I (0,25% in 0,8g KBr pellets), a) before drying, b) after drying at 140°C, c) after calcination at 600°C.

carried out, using the diffractometer DRON-1, USSR. The diffraction patterns are shown on Fig. 4.

The specific BET surface area data were obtained by the conventional BET method, basing on nitrogen adsorption at 77°K on samples predried at 110°C before being weighed up for the BET measurement. Using the nitrogen adsorption and desorption isotherms the average pore diameters of the different kinds of white rubber fillers were calculated by the method of Cranston and Incley[6].

Fig. 5, prepared on the basis of Tab.1 serves to show the main differences between the various kinds of active silicas. In the middle part of the figure values found for the white rubber fillers are demonstrated. The line drawn from

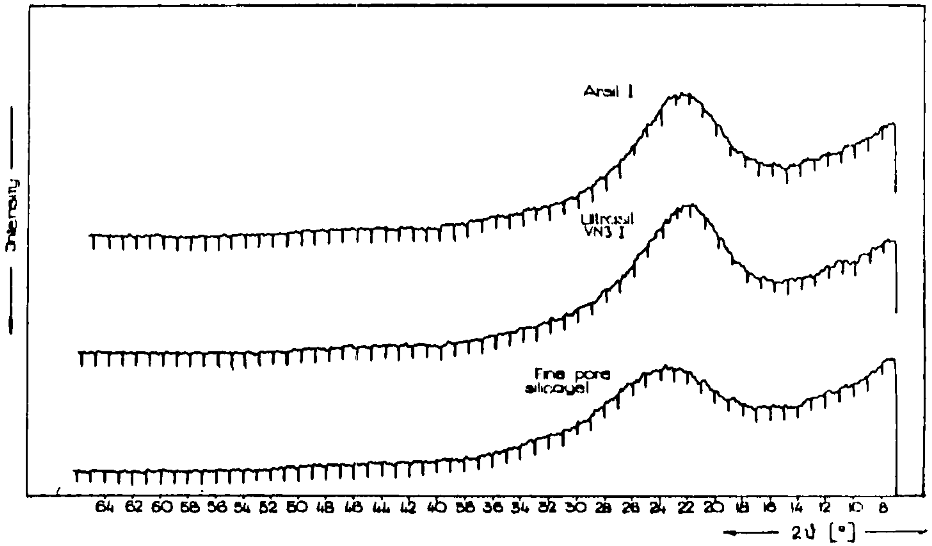

Fig. 4. Diffraction patterns of three samples of active silicas

point to point shows the direction of changes of properties from one kind of silica to the other.

RESULTS AND DISCUSSION

It was shown, that the intensity of the Si-O vibration bands of active silicas depends on the kind of silica. The samples may be arranged in the following order due to the increasing sharpness of the 1110 cm^{-1} absorption band: fine pore silica gel, large pore silica gel, beer stabilizer Piwator, and close to one another the white rubber fillers Ultrasil, Aerosil and Arsil. The increase of band sharpness may be explained by a higher degree of structure order, as the equal

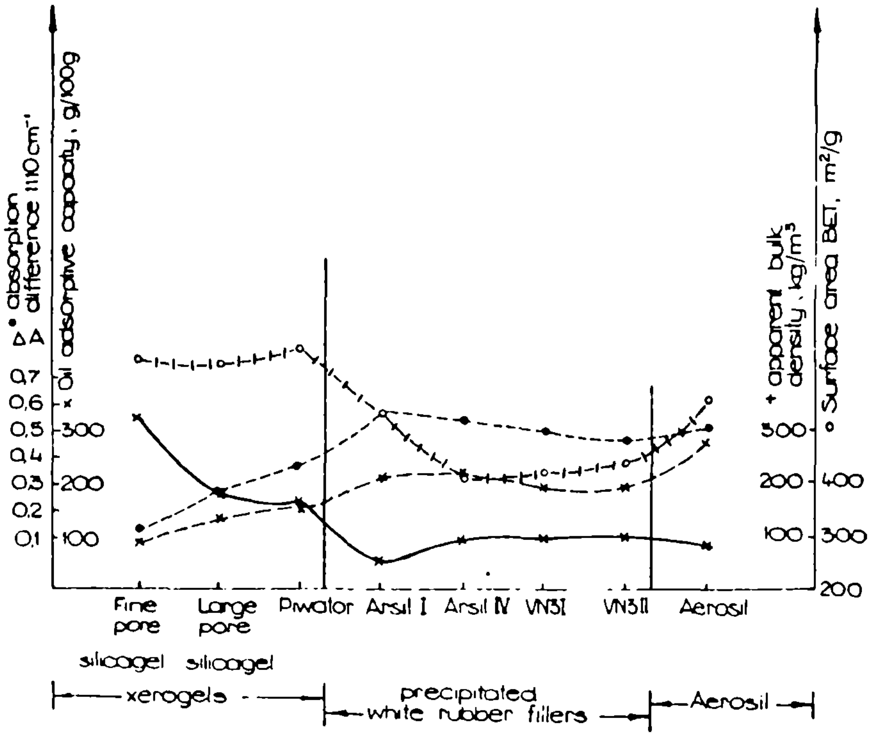

Fig. 5. The variation of some physicochemical properties of different kinds of active silicas.

coupling of vibrations of identical sites is the reason for well defined vibration frequencies, reflected by descreet vibration bands.

Similar conclusions as to the structure order may be drawn on hand of the halfwidths of bands of the X-ray diffraction patterns (Fig.4), and on hand of the shape of the 960 cm^{-1} i.r. bands. The last were attributed by Hino and Sato to OH groups hydrogen bonded with molecular water[7]. The X-ray diffraction pattern of each of the three samples has one broad band, characteristic for amorphous materials. But the differences in the half widths of bands suggest a more or less ordered structure. Ultrasil VN3 (I) and Arsil I show similar values of the band half width, 39 mm and 38 mm respectively. The diffraction band of the fine pore silica gel, which accordingly to the i.r. spectra is supposed to be more amorphous, has a much larger half width of 49,5 mm.

The shape of the 960 cm^{-1} OH band, which is more discreet in case of the precipitated rubber fillers than of beer stabilizers and fine pore silicagels may also be explained by a more or less ordered arrangement of OH groups, depending on the whole structure order. After calcination of samples at 600°C the 960 cm^{-1} band disappears, prowing its connection with the hydroxyl groups.

The values of adsorptive capacities are higher for white rubber fillers than for silica gels, despite of lower surface areas. The variation in oil adsorptive capacities of different kinds of silicas tends to parallel the intensities of i.r. bands (Fig. 5). This leads to the conclusion, that factors, promoting the "crystallinity" during the synthesis will likewise favour increased pore volums.

This statement may be supported by another conclusion, that the increase of structure order of active silicas causes a decrease in their bulk density.

Ultrasil, Arsil and Aerosil have high adsorptive capacities and show similar intensities of the Si-O bands of their i.r. spectra and also similar apparent bulk densities and average pore diameters. But the spectrum of Aerosil is distinguished by the lack of the 960 cm^{-1} hydroxyl absorption band.

REFERENCES

1. J.H.De Boer, J.M.Vleeskens, Proc. Koninkl. Ned. Akad. Wetenschap, Ser. B, 61, 2 /1958/;
2. J.A.Hockey, Chem. Ind. /London/, 57 /1965/;
3. L.R.Snyder, J.W.Ward, J.Phys.Chem., 70 /12/, 3941 /1966/;
4. L.Firlus, Z.Dacy, K.Szyszka, G.Kuśnierczyk, Pol.Pat. 91219 /1973/;
5. L.Firlus, Z.Dacy, L.Pietrzyk, J.Gawron, Pol.Pat. 86494 /1973/;
6. R.W.Cranston, F.A.Incley, Advances in Catalysis, IX, 143 /1957/;
7. M.Hino, T.Sato, Bull. Chem. Soc.Jap., 44, 33 /1971/.

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