PROPERTIES OF PLASMA SILICA POWDERS USED TO SAPO MOLECULAR SIEVE SYNTHESIS

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Ultra pure silica particles <4 nm generated in a capacitively coupled rf plasma (CCP) and deposited within the reactor at high quenching rates of the plasma activated species form agglomerates with rugged, reactive surface areas as well as with a great number of internal structure bonded hydroxyl groups. These particle properties point to a higher solubility of plasma silica powders advantageous to their availability at the synthesis of molecular sieves.

INTRODUCTION

The kind of the silica source influences apparently the number and the nature of acidic sites and therefore the catalytic activity and selectivity of silicoaluminophosphate molecular sieves (SAPO) [1,2], interesting crystalline microporous solids for separation and catalytic processes [3]. As reported in the previous studies [1,2], the use of plasma-chemically generated silica powders results in a increasing isomorphous incorporation of silicon into the SAPO-31 framework connected with a remarkable high Broensted acidity of the synthesized molecular sieves. In contrast, only a small part of the silicon from Aerosil manufactured by flame hydrolysis [4] is inserted into the SAPO frame-

work. The larger parts exist as silica isles or as $SiSi_4$-clusters within the SAPO pore system.

The present paper is a contribution to the search for physical and chemical properties of these plasma silica powders supposed as a cause of the behaviour described above.

EXPERIMENTAL

Briefly, the silica powders are generated in a capacitively coupled rf plasma (CCP) [5] by reaction of tetrachlorosilane and oxygen corresponding to $SiCl_4 + O_2 \rightarrow SiO_2 + 2Cl_2$. Two copper electrodes couple the rf energy of a 1 kW generator (4MHz, Steremat Berlin) into an air cooled quartz reactor (l=50cm, ∅= 3cm). Generally, the mixture of the plasma gas argon (D_{Ar}=7.1 mol/h) and the reactants ($SiCl_4$=0.22 mol/h, D_{O2}=0.31 mol/h) is fed above the plasma column. The quenching rate and the residence time of reactants are in the ranges $10^5<T/K\cdot s^{-1}<10^6$ and $10^{-2}<t_V/s^{-1}<10^{-1}$, respectively. The powders deposited in the reactor (13-06), in the following quenching section (13-07), and on a filter (13-10) as well as an Aerosil-200 reference sample are analyzed by electron microscopy (TEM, BS 500 Tesla), thermogravimetry (TG, derivatograph MOM Budapest), infrared spectroscopy (IR, FTIR spectrometer IFS 66, IFS 66V, Bruker), BET-specific surface area (Milestone 200 Report Generator, Fisons Instruments), and optical emission spectrometry (OES, ICP emission spectrometer JY 70P/Jobin Yvon).

RESULTS AND DISCUSSION

There are distinct differences between the plasma silica powders and the Aerosil. The total amount of metallic impurities measured by OES in the plasma powder is <10 ppm compared to Aerosil with about 57 ppm. The TEM grain sizes of 10-20 nm of the non-structured Aerosil particles are in good agreement with the BET values of S_{spec}=247 m^2/g and confirm its nonporosity [6]. Especially, those plasma powders deposited already within the reactor (13-06) have particle modifications differing from Aerosil. With residence times <10 ms of the reactive species in the upper plasma region, the great supply of [Si-R] radicals (R = Cl, O) as well as its insertion into the clusters lead to a permanent "renewal" of reactive sites on the surface area of the growing particles, evidently. This process freezed by the fast quenching rate of about $\Delta T/\Delta t \sim 10^6$ K/s is rate-determining as against the parallel running intra- an interparticle change of the structure. With the quenching, a mutual saturation of the reactive valences at the surface area of neighbouring particles takes place by linking of clusters <4 nm forming agglomerates (10 - 20 nm) like a "blackberry" [7]. With increasing residence time, a multiplied number of collisions takes place between the particles which cover in the plasma column regions with poorer [Si-R] radical concentrations moving towards zero finally. The reactions on the surface area are now determined by internal rearrangement and recombination processes and the particle growth takes place almost by smelting of the

agglomerated particles. Both processes stabilize the smooth surface structure of the fused spherical particles of 20-70 nm (13-07, 13-10).

The measured specific surface area of 206 m^2/g for the sample 13-06 is inconsistent with the dominating structures <4 nm. Possibly, a cause of this is to see in the packing density of those clusters within the "blackberries". If the coordination number is ≥6, more than 30% of the surface would not be available to the adsorbed nitrogen.

This is confirmed by the thermogravimetric results (Fig. 1). In accordance with the bend of the TG curve at T=150°C, physisorbed water is splitted off to T=150°C [8,9]. The observed mass losses at T>150°C are explainable by the desorption of chemisorbed hydroxyl groups [8,10]. The measured Aerosil data are theoretically verified by assumption a hydroxyl group density of 4 OH/nm^2 [6]. However, differences between experimental data and theoretical values of the plasma powders appear in the range of chemisorbed hydroxyl groups at sample 13-06, in particular. Opposite to the measured 9 wt% mass loss of the sample 13-06 corresponding to a hydroxyl group density of 15.6 OH/nm^2, only a value of 2.3 wt% is calculated on the base of the measured specific surface area of 206 m^2/g. An assumption of a value $S_{spec} \geq 650$ m^2/g corresponding to 4 nm particles could explain this difference, provided, the packing of particles is so dense that the volume between the grains are passable only for water molecules but not for nitrogen. In this sense, the surface area of the sample 13-06 is mainly made of internal structural bonded hydroxyl groups.

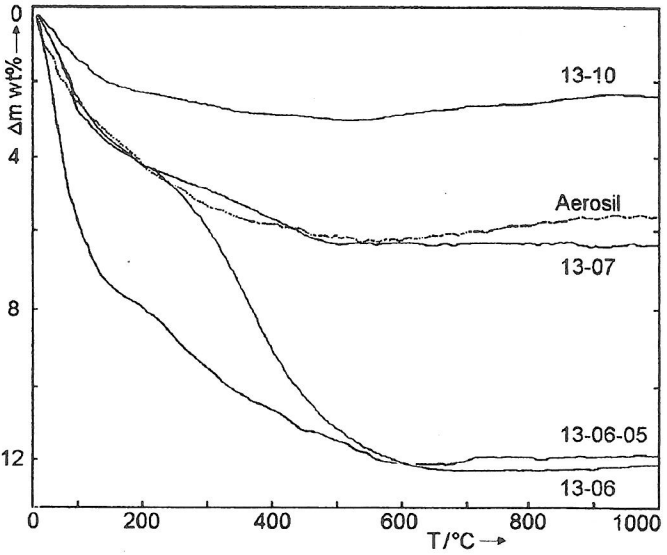


Fig. 1: Thermogravimetrical analysis of the powders (sample mass: 20 mg, rate of annealing: 10 K/min, atmosphere: air)

Also the strong increase of the desorbing water to 150°C with unchanged total mass loss of the aged sample 13-06 points to a high reactivity and to the existence of metastable surface structures. Because of the closed storage of this sample, foreign

influences are excluded. So this change can be interpreted only by rearrangement in the particles. As shown schematically in Fig. 2, the fresh hydroxylated, strong rugged surface area has ranges of small curvatures. Between these sites consisting of geminal or triple OH-groups saturated silicon atoms [11] and regions with negative curvatures or points of particle contact, dissolution and precipitation reactions by the orthosilicic acid take place. The number of chemisorbed hydroxyl groups diminishes in favour of the forming of free water. The possibility of such a process has been discussed in [11].

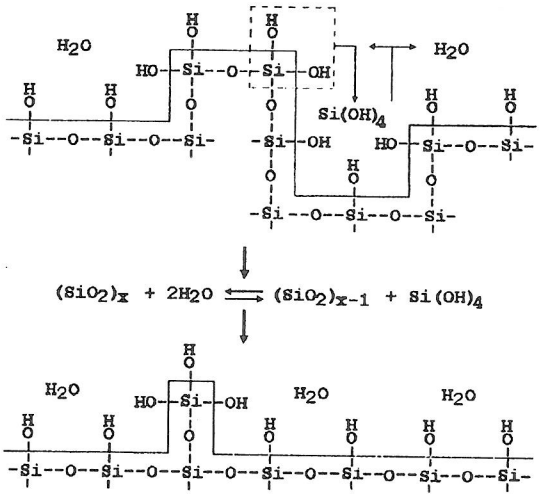
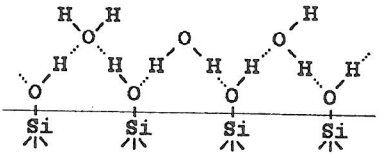


Fig. 2: Scheme of the migration of hydroxyl groups at the surface area of the plasma powders

The appearence of correlating infrared bands at 3650 cm^{-1} and 950 cm^{-1} [12] at the sample 13-06 (Fig. 3) supports the assumption of structural bonded water as an explanation of the high hydroxyl group density. Since the hydroxyl groups corresponding to the band at 3650 cm^{-1} do not react with deuterium oxide and boron chloride, several authors conclude that this band is assigned to stretching vibrations of internal hydrogen bonded silanols [7,9] or to the stretching mode of silanols perturbed by interparticle contact [13]. An annealing of the powder leads to the forming of Si-O-Si bridges at the contact sites under separation of water; the desorption of which is impeded just by those siloxan bridges. Therefore, this water is detectable in the powder still as residue at temperatures of 1000°C [14]. The Si-O(H) stretching mode at 950 cm^{-1} of directly to silicon bounded hydroxyl groups [15] also indicates interacting hydroxyl groups because no hydroxyl stretching modes of free silanol groups at about 3750 cm^{-1} are observed in the spectra of plasma powders. Decreasing and regeneration of the band at 950 cm^{-1} with annealing and cooling of the sample 13-06 in a temperature range of 0 - 400°C indicate an interaction of weakly bonded hydroxyl groups with the silicon surface atoms like a physisorption of water over hydrogen bridges to silanol groups. Considerable amounts of water are absorbed on a silanol surface area if the surface complexes can form two hydrogen bonds between the Si-OH sites and water as follows [16]:



The rugged surface area or the neighbourhood of the interparticle contact sites of the plasma powders, are preferred sites for the formation of such structures. As a result of the creating of hydrogen bridge bonds between water molecules and silanol groups multiplies the number of the linked silanol groups which desorb water already at low temperatures. These statements are supported by the behaviour of the Si-O(Si) stretching mode of the silica framework: In the spectrum of sample 13-06 at which silanol groups at 950 cm^{-1} absorb, the Si-O(Si) band lies 15 cm^{-1} lower (1100 cm^{-1}) compared to the without these silanol groups (13-07,-10, Aerosil) and to the spectra of the corresponding annealed dehydroxylated samples.

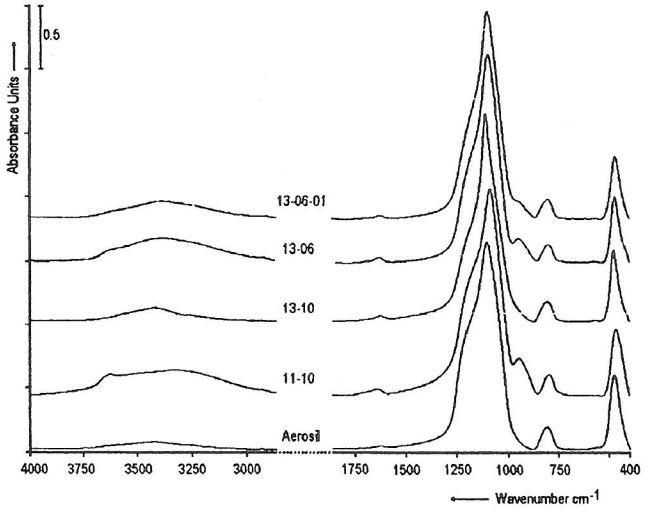


Fig. 3: Infrared spectra of silica plasma powders and of Aerosil (sample 13-06-01 is the powder 13-06 immediately after the synthesis, the spectra are base line corrected and are converted to the same concentration)

It was supposed in [1] that the increasing isomorphous insertion of silicon from plasma silica powders into the SAPO framework is connected with the existence of monomeric silicic acid during the gelation process. There are indications for a higher solubility of the plasma silica particles: the particle size <4 nm, the reactive surface area sites, the high internal hydroxylated surface area of the agglomerates as well as the high purity of the plasma powders. The influence of such particle properties at the solubility is discussed detailed in [8]. The great relevance of the silica solubility as the rate determining step is emphasized also in [17] in connection with the hydrothermal reaction of silica and calcium hydroxide.

CONCLUSION

Freezed rugged reactive surface areas and a great number of structure bonded hydroxyl groups of spherical agglomerates from very pure silica clusters <4 nm generated in a rf plasma could be a cause for an increased incorporation of silicon atoms into the framework of the molecular sieve by higher solubility and availability of this plasma silica.

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