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Surface Characterization of Silica Modified with Aminosilane Compounds

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Adsorption behaviors, IR spectroscopy and surface electric properties were studied on the surfaces of well-defined mesoporous silica gels modified with triethoxy(3-aminopropyl)silane (TAS) and [3-(dimethylamino)propyl]diethoxymethylsilane (DDS). Surface free silanol groups react with ethoxyl groups of these compounds rigidly. Isoelectric points and points of zero charge of modified silicas shift from pH 3 of pure material to alkali, but DDS-modified silica gels dissolve themselves in aqueous phase because of their strong alkali environment.

Silica gels modified with a large variety of silane derivatives are used for the liquid/solid and gas/solid adsorption chromatography,[1] and there are substantial studies such as states of modifications and adsorption behaviors.[2,3] However, the surfaces of silica gels in these studies were usually not well-characterized in view of, for example, the species and population of surface silanol groups which are substituted with various modifying agents and thence the degree of surface coverage of functional groups per unit area. Therefore, there are still some ambiguities on the state of modified compounds on the surface. On this point of view, surface characterization of ethoxylated mesoporous silica gels was carried out in this laboratory with the result that one ethanol molecule reacts with one free silanol group which covers the surface with a population of 3/nm^2.[4]

The purpose of this report is to clarify details of surface modification with coupling agents which have plural number of reacting functional groups per molecule such as triethoxy(3-aminopropyl)silane (TAS) and [3-(dimethylamino)propyl]diethoxymethylsilane (DDS) by means of well-characterized mesoporous silica gels as a starting material.

Experimental

Materials. Thin transparent plates of mesoporous silica gels of about 0.1 to 0.05 mm thick were made as mentioned elsewhere.[4] Specific surface areas (A_s), pore volumes (V_p) and mean pore radii (r_p) of sample S1 were 718 m^2 g^{-1} 0.63 cm^3 g^{-1} and 1.8 nm respectively. Surfaces of these materials were modified with TAS and DDS by immersing the material in toluene solution of these coupling agents in various concentrations relative to total amount of free hydroxyl groups in these silica gels, and by warming at 323 K for 5 h. The products were washed with toluene and ethanol and dried in vacuo at room temperature.

Adsorption Properties. Specific surface areas, pore volumes and mean pore radii were obtained from nitrogen isotherms using B. E. T. and Cranston-Inkley equations.

IR Spectroscopy. Ft-nir spectrometer of Digilab FTS15E with a PbSe detector was used with 2 cm^{-1} resolution, in the range from room temperature to about 1000 K in vacuo.

Chemical Analysis. The amount of carbon and nitrogen atoms contained in modified samples was measured both by simultaneous TG-DTA and by CHN elements analyzer of Yanagimoto Co. Total number of OH groups, N_{OH}/nm^2, being obtained from ignition loss between 423 and 1373 K were 7.2 and 6.5 for S1 and S2 sillca gels respectively.

Surface Electric Charges. ζ Potentials were measured with ground powders suspended and pH-equilibrated in water by means of ζ meter of Penkem Co. model 501. Points of zero charges (pzc) were estimated from pH change caused by adding a known amount of hydrogen chloride or potassium hydroxide to the solution obtained by immersing 100 mg of powdered samples in the 0.1 mol l^{-1} solution of potassium chloride under nitrogen gas stream at 302.3 K.

Results and Discussion

The nitrogen adsorption isotherms of original and modified samples with TAS are typical to mesoporous materials as is shown in Fig. 1 in which N_n is the number of nitrogen atoms of TAS reacted with the surface per unit surface area and is equal to the

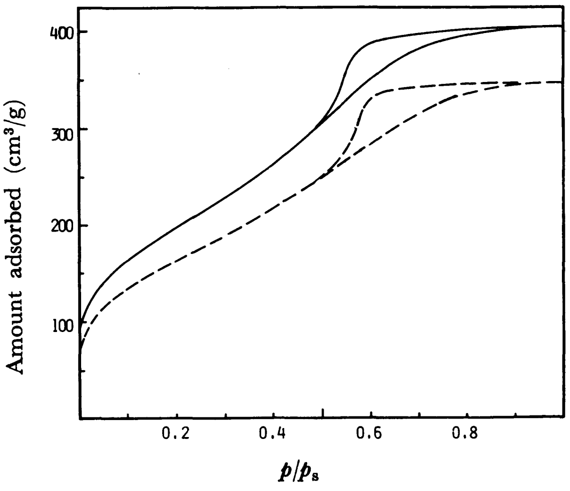


Fig. 1. The nitrogen adsorption isotherms of sample S1 (full line) and that modified with TAS to N_n= 0.49/nm^2 (broken line).

number of modified functional groups. Pore sizes are fairly uniform looking from pore size distribution curves in Fig. 2 with smaller maximum for larger amount of modification with TAS. Specific surface areas (A_s m^2 g^{-1}) and pore volumes (V_p ml g^{-1}) being computed from nitrogen gas adsorption isotherms of sample S2 decreased as the degree of modification with TAS and DDS was increased, whereas it was rather unusual to see that mean pore radii (r_p nm) did not decrease significantly as is seen in Table 1. The same tendency was observed with sample Sl.

The monolayer capacity of adsorbed water decreases by increasing degree of modification, such as from 4.7 water molecules/nm^2 to 1.5/nm^2 on sample modified with DDS to N_n=0.7. This shows that the sample became less hydrophilic by DDS modification, which was also true in case of TAS modification.

The reaction of these coupling agents on silica surface proceeds further to give the amount reacted much higher than monolayer of these substituted functional groups such as N_n=1.0. The ratio of nitrogen atoms to carbon atoms contained in silica gels after reaction was nearly equal to 0.7:3.0, as is seen in Fig. 3. This value is smaller than the ratio of these atoms in one molecule (1.0:3.0). This indicates that roughly one out of three ethoxy groups of a molecule did not react with surface silanol groups, the reason for which was explained by IR spectroscopy as is mentioned later. A_s, V_p, and r_p become smaller because of pore filling. However, the amount of these agents enough to cover the surface and form monolayer can not be precisely estimated from these results only.

Original mesoporous silica gels have mainly three types of silanol groups such as free silanol groups having a surface concentration of about 3/nm, inner OH groups and interparticle hydrogen-bonded silanol groups whose wave numbers are 3740, 3670 and about 3500 cm^{-1} respectively as was discussed elsewhere,[4] and as is partly seen in the ir spectra of unmodified sample Sl in Fig. 4. After modifying this sample with TAS and DDS, the absorbance of OH fundamental stretching band of free silanol groups decreases, and C–H and N–H bands in case of TAS increased. The absorbances of N–H band in case of TAS were proportional to the amount of nitrogen atoms contained in the sample, but free OH band disappears at nearly N_n=0.7 as is seen in Fig. 5. This was also true in case of DDS. This may be interpreted as that roughly two surface free silanol groups reacted with TAS or DDS, which agrees with the above mentioned result. The amino or dimethylamino groups of the substituted functional groups may be hydrogen-bonded to the

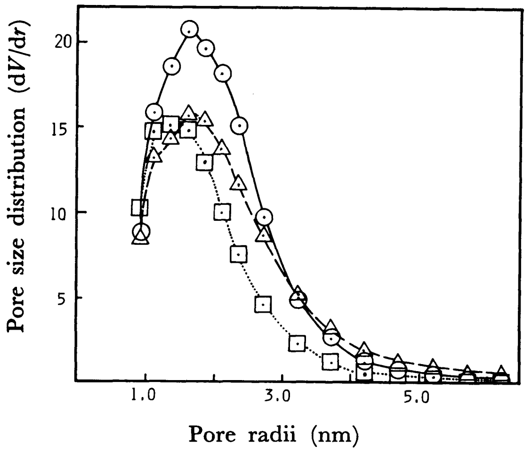


Fig. 2. Pore size distribution curves of sample S1 (circles), those modified with TAS to N_n=0.49 (triangles) and N_n=1.54 (squares).

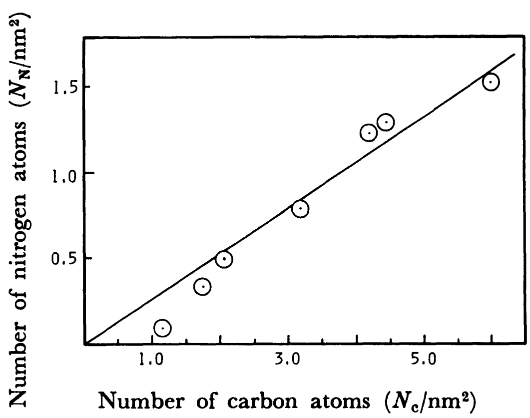


Fig. 3. The relation between number of nitrogen and carbon atoms contained in sample S1 modified with TAS.

Table 1. Nitrogen BET Specific Surface Areas (As) Pore Volumes (V_p) and Mean Pore Radii (r_p) of Sample S2 as the Function of Numbers of Modified Functional Groups Per Unit Surface Area

Number of substituted functional groups/N_n/nm^2		A_s m^2/g	B.E.T. parameter c	V_p/cm^3/g	r_p/nm
—	0	706	93	0.71	2.0
TAS	0.32	502	74	0.52	2.1
TAS	0.82	443	73	0.40	1.8
DDS	0.27	525	64	0.52	2.0
DDS	0.52	489	39	0.57	2.3
DDS	0.90	413	32	0.43	2.1

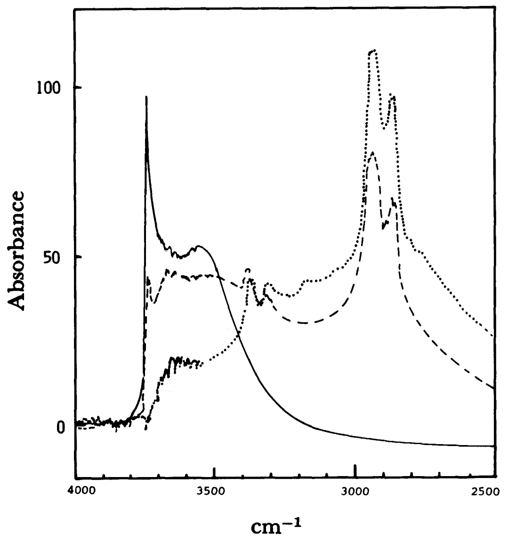
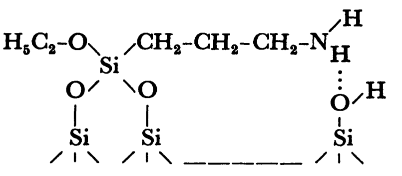


Fig. 4. IR spectra of sample S1 (full line), those modified with TAS to $N_n = 0.49$ (broken line), and to $N_n = 1.54$ (dotted line).

remaining one free silanol group as follows.



Thus, free silanol band disappeared and all three free silanol groups per nm^2 might have been used to form a monomolecular layer of functional groups. Modifying functional groups more than monolayer seem to react with each other forming some kind of polymers and lie over these modified surfaces to fill pores.

ζ Potentials and pzc were mearsured on these original and modified samples as the function of pH. The values of isoelectric points (iep) and pzc of the same sample agreed well to each other and were higher by increasing the amount of modification. Surface electric charges changed greatly by amine modification as one can expect. The iep and pzc of TAS modified samples were both about 8.0 and were stable for a prolonged period of time. On the other hand, initial values of iep and pzc of the DDS modified sample were equal to about 9.8 which is much higher than that of TAS, but went down to about 8.5 in 1 d. In this case, particles of this material dispersed in distilled water at room temperature are dissolved and disappeared after a few hours under microscope because of high pH produced by strong basicity of its surface. The free OH band emerged again after immersing this DDS-modified material in distilled water for several hours. These materials absorb alkyl halides irreversibly as is reported elsewhere.[5]

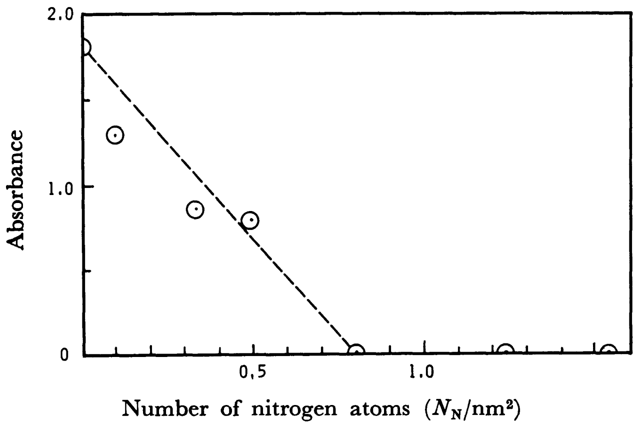


Fig. 5. The absorbance of O–H band as a function of number of nitrogen atoms contained in sample S1.

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