Surface and Structural Properties of Silica Gels Used in High Performance Liquid Chromatography

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SURFACE AND STRUCTURAL PROPERTIES OF SILICA GELS USED IN HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

Complete nitrogen adsorption-desorption isotherms were measured over the entire pressure range including the region of very low pressures for a series of silica gels used in high performance liquid chromatography. In addition to standard characterization of the silicas studied, which included the evaluation of the specific surface area and the total pore volume, the experimental adsorption isotherms were used to calculate the adsorption energy distributions and the pore volume distributions by employing an advanced numerical algorithm based on the regularization method. For most silica samples studied, the resulting energy distributions are similar indicating that their surface properties are analogous. For some silicas, which are able to chemisorb greater amounts of water as shown by supplementary thermogravimetric studies, the adsorption energy distributions are different. Analysis, of the resulting pore volume distributions for most silicas studied, shows a relatively narrow range of mesopores and no substantial evidence for the presence of micropores.

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INTRODUCTION

Porous silicas are widely applied in many areas of modern science and technology, especially in sorption-based separations, chromatography and catalysis.[1,2]   They are extensively used in gas (GC) and liquid (LC) chromatography due to their high mechanical, chemical and thermal stability. Silica gels can be easily modified by bonding different types of ligands to their surface.[3,4]   Their high surface reactivity provides a unique opportunity for preparing various stationary phases of desired chemical properties which enable even very involved and refined separations.

Chromatographic performance of silica packings and silica-based stationary phases depends significantly on the surface and structural properties of the silica particles. The surface properties in turn are determined by the surface roughness as well as by surface silanols, siloxane groups and various bonded impurities (mostly metal oxides).   The structural properties are determined by the presence of pores of different shape and size and by their connectivity. In order to control the synthesis of chemically bonded phases, the starting silica needs to be well characterized.[4]

An appropriate characterization of silicas is crucial in selecting porous supports suitable to prepare chemically bonded phases for gas and liquid chromatographic separations. In the current work, a series of porous silicas used in high performance liquid chromatography is characterized in terms of the adsorption energy distribution evaluated from the low-pressure nitrogen adsorption isotherm data. In addition, their porous structures are determined on the basis of the complete nitrogen adsorption isotherms.

METHODS

Sorption Measurements

Eight commercial chromatographic silicas were selected to carry out extensive sorption studies. Prior to performing sorption measurements silica gels were degassed at 473 K for 2 hours under the vacuum of approximately 10^{-4} Torr by using the degas port of the sorption analyzer. High purity (99.99 %) nitrogen was used to carry out sorption measurements. Complete adsorption-desorption isotherms were measured by ASAP 2010 volumetric sorption   instrument from Micromeritics (Norcross,GA). This instrument
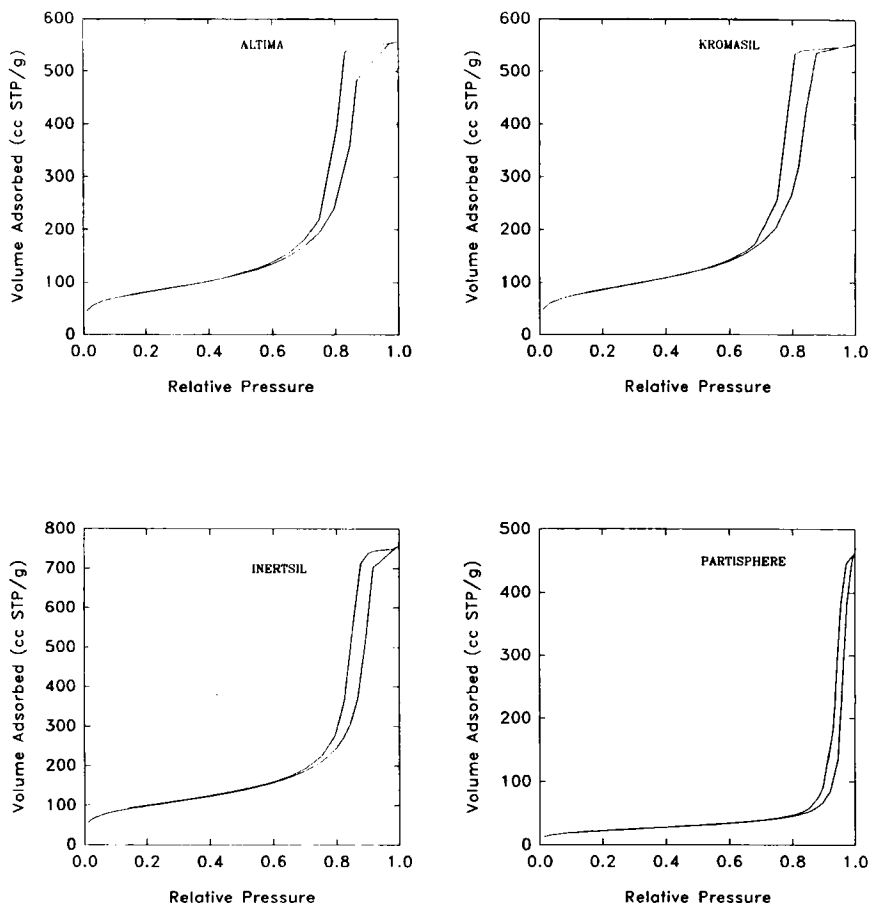
Figure 1. Nitrogen adsorption-desorption isotherms on Altima, Inertsil, Kromasil and Partisphere at 77.35 K.

allows to perform high-resolution adsorption measurements over a wide range of relative pressures from 10^{-6} to 1. The adsorption-desorption isotherms are shown in Figures 1 and 2.
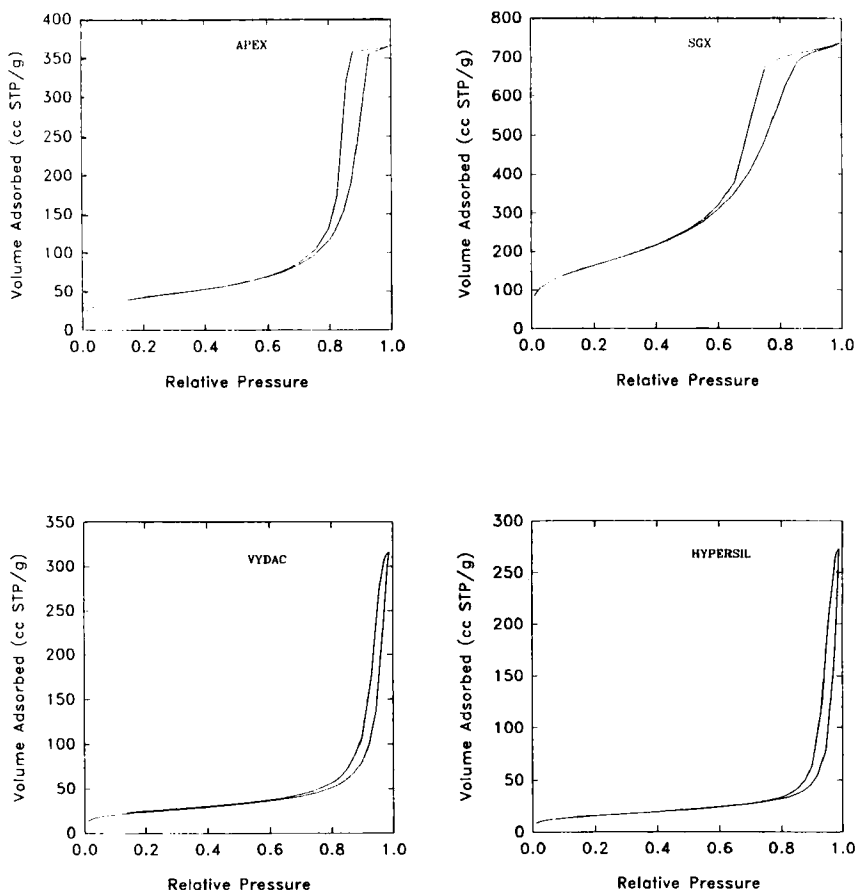
Figure 2. Nitrogen adsorption-desorption isotherms on Apex, SGX, Vydac and Hypersil at 77.35K.

Standard Characterization

The low temperature nitrogen adsorption-desorption isotherms were used to evaluate such standard quantities as the BET specific surface area, the external surface area, the total pore volume and the micropore volume.[5,6] The methods of calculation of these quantities from adsorption data are well described in basic adsorption books.[6] The total specific surface area was evaluated according to the well-known BET equation from nitrogen adsorption data at the relative pressure range from 0.05 to 0.25. The total pore volume was

estimated by converting the volume adsorbed at the relative pressure of 0.975 to the volume of liquid adsorbate. The external (mesopore) surface area and the micropore volume were evaluated from the t-plot method, which is based on the comparison of the adsorption isotherm for the sample studied with the standard isotherm measured on a reference nonporous material.[6] In the latter method, the standard isotherm on the reference solid is expressed in terms of the thickness of the adsorbed layer t. The intercept and slope of the linear segment of the t-plot was used to evaluate the micropore volume and the external surface area, respectively.

Calculation of the Pore Volume Distribution

Nitrogen adsorption isotherms at 77.5 K were used to obtain information about structural heterogeneity of the silicas studied. The pore volume distribution $J(x)$ is related to the volume adsorbed V through the following integral equation:[5,7]

$$V(p) = V_t \int_\Omega \theta_x (p, x) J(x) dx \qquad (1)$$

where V_t denotes the maximum volume adsorbed, p is the equilibrium pressure, $J(x)dx$ denotes the fraction of pores between widths x and $x+dx$, $\theta_x (p,x)$ stands for the local adsorption isotherm in the pores of the width x, and Ω denotes the integration region with respect to x. The pore volume distribution $J(x)$ was calculated by employing the regularization method[8] to invert the integral Eq. 1 for *a priori* assumed local adsorption model. Since there is no analytical equation to describe the complete volume filling of uniform pores, the local adsorption isotherm in Eq. 1 was calculated via the density functional theory.[9-11]
Olivier et al.[12] combined the density functional theory approach[11] with the regularization procedure[8] in order to elaborate an advanced numerical method (DFT software) for calculating the pore volume distribution from the entire adsorption isotherm. In the current work, this method was used to calculate the incremental pore volume distribution function, from which the cumulative pore volume distribution can be obtained by performing appropriate summations of incremental pore volumes. Differentiation of the latter distribution leads to the differential pore volume distribution $J(x)$.

Calculation of the Adsorption Energy Distribution

The energy distribution $F(U)$ was calculated from low pressure nitrogen adsorption data by inverting the following integral equation,[7] which is analogous to Eq. 1:

$$\Theta(p) = \Theta_1 \int_\Delta (p, U) F(U) dU \qquad (2)$$

where $\Theta(p)$ is the relative adsorption in the submonolayer range, which is the ratio of the adsorbed amount to the BET monolayer capacity; U is the adsorption energy, $\Theta_1(p, U)$ is the local adsorption isotherm as a function of the adsorption energy, Δ is the integration region and $F(U)dU$ denotes the fraction of the surface with adsorption energies between U and $U+dU$. To invert the integral Eq. 2 with respect to the energy distribution function $F(U)$ one needs to assume a local adsorption model. In the current work, the well-known Fowler-Guggenheim (FG) equation, which describes the localized monolayer adsorption with lateral interactions, was used:

$$\theta_1(p, U) = \frac{Kp \exp(zw\Theta / kT)}{1 + Kp \exp(zw\Theta / kT)} \qquad (3)$$

with:

$$K = K_0(T) \exp(U / kT) \qquad (4)$$

where Θ is the relative adsorption defined above, z stands for the number of the nearest neighbors of a molecule in the monolayer and w is the interaction energy between nearest neighbors. K is the Langmuir constant for adsorption on monoenergetic sites and the pre-exponential factor $K_0(T)$ is expressed in terms of the partition functions for an isolated molecule in the gas and surface phases.[7] The above factor was estimated according to the Adamson method.[13] The FG Eq. 3 describes the local adsorption with lateral interactions (where w is the interaction energy and z is the number of nearest neighbors) on the surfaces of random distribution of adsorption sites, which appears to be realistic for silica surfaces.[14] The energy distributions for the silicas studied were calculated by employing the regularization method (INTEG program)[8] to invert Eq. 2 with respect to F(U). The interaction paremeters $z = 4$ and $w / k = 95K$ were assumed.

RESULTS AND DISCUSSION

Complete adsorption-desorption isotherms, measured at 77.35 K for all silicas studied, are shown in Figures 1 and 2. These isotherms can be considered as type IV according to the common classification of the gas/solid adsorption isotherms.[6] The shape of the adsorption isotherms for all samples reflects monolayer adsorption followed by the multilayer formation and

subsequently by the capillary condensation, which is the source of the hysteresis loop in the higher pressure region. Except the SGX silica, the hysteresis loops for the other silicas show type H1 with some resemblance to type H2 according to the IUPAC classification.[6,15,16] The model H1 hysteresis loop has the adsorption and desorption branches almost vertical and nearly parallel over a considerable range of pressures.[6] This type of hysteresis loop is characteristic for agglomerates or compacts of spheroidal particles of similar size arranged in a fairly uniform way.

Hysteresis loops for Partisphere, Hypersil and Vydac resemble type H1 and are located in the range of relative pressures between 0.8 and 1.0, which indicates that their porous structure contains mostly large mesopores and small macropores. Note that according to the IUPAC recommendations,[15,16] the pores are clasified into micropores (widths below 2 nm), mesopores (widths between 2-50 nm) and macropores (widths above 50 nm).

For the remaining silicas the hysteresis loop starts at the relative pressure range between 0.6 and 0.7, and tends to be similar to the loop type H2, which is often observed for silica gels of relatively narrow mesopore distribution with maximum about 10 nm. For the SGX silica the hysteresis loop exhibits type H2 and differs significantly from the hysteresis loops for other samples studied.

A standard numerical analysis of nitrogen adsorption isotherms was carried out in order to provide a quantitative estimation of the BET specific surface area S_{BET}, the total pore volume V_t and the average pore diameter w. The latter was calculated on the basis of the incremental pore volume distributions obtained by using the DFT software.[12] They are summarized in Table 1 and occur to be significantly different from those reported in the manufacturer catalogs, which provide average values for a given brand of the silica.

While the BET specific surface areas are in a reasonable agreement with the available catalog data, the average pore widths show greater discrepancies. It is known that the surface and structural properties of two batches of the same brand of silica can differ significantly. The latter properties also depend on the pretreatment methods and analysis conditions. Moreover, there may be some disagreement between results obtained on the basis of different methods.

In spite of the above comments, Table 1 provides valuable information about surface and structural differences among the silicas studied in the current work because all adsorption measurements were carried out under the same conditions.
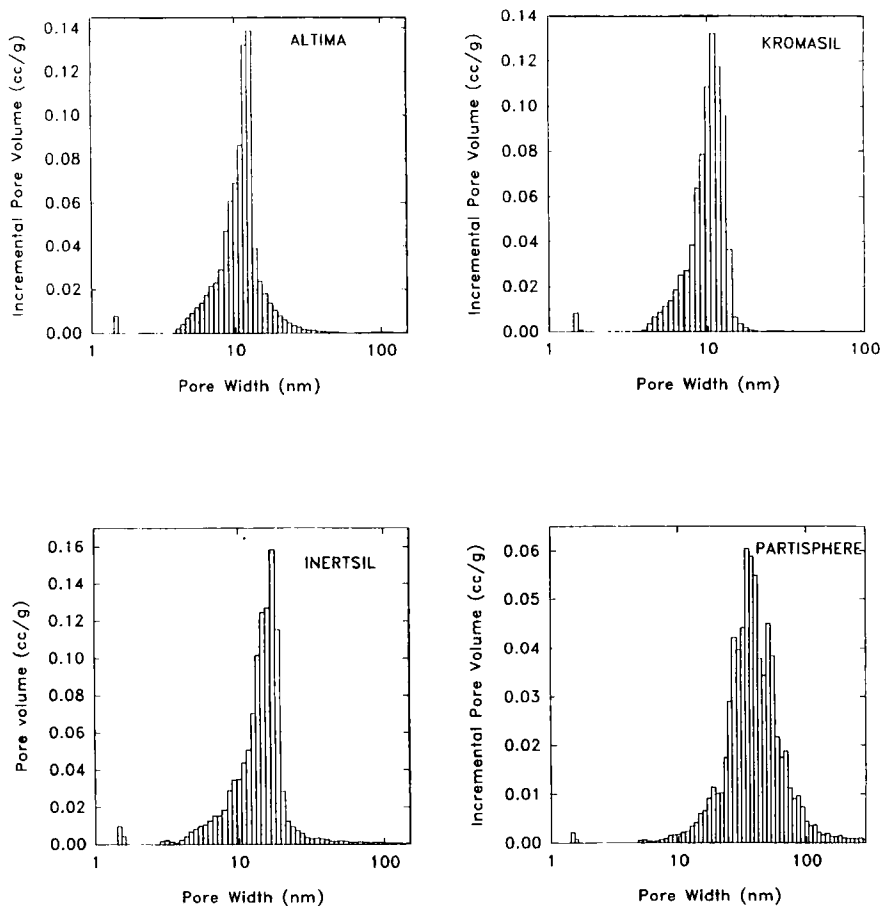
Figure 3. Incremental pore volume distributions for Altima, Inertsil, Kromasil and Partisphere calculated from the entire nitrogen adsorption isotherms.

As can be seen in Table 1 the silicas under study showed different surface and structural characteristics. Their BET specific surface areas vary from 60 to 600 m^2/g. The specific surface areas of Hypersil, Partisphere and Vydac are about 60-80 m^2/g, whereas Kromasil, Inertsil and Altima exhibit the surface area about 300 m^2/g. The surface area of the SGX silica is about 600 m^2/g. The t-plot analysis showed no substantial evidence for the presence of fine pores (widths below 2 nm) in the silicas studied except SGX, which possesses a small fraction of micropores. The total pore volumes of the silicas studied are
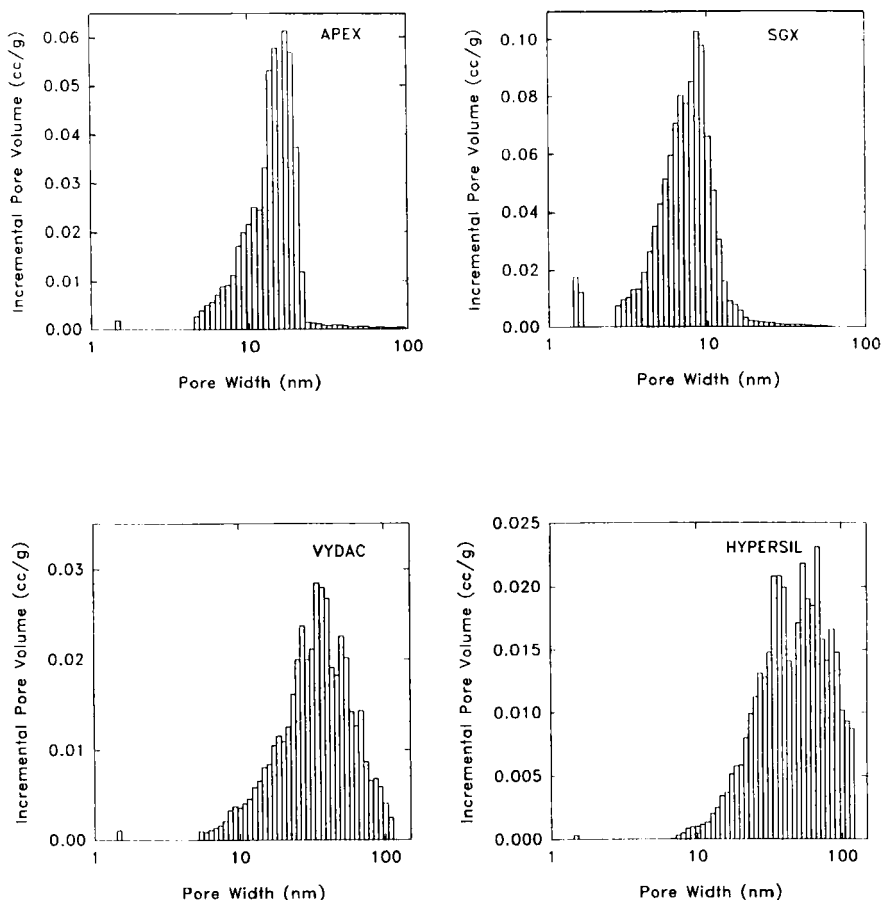
Figure 4. Incremental pore volume distributions for Apex, SGX, Vydac and Hypersil calculated from the entire nitrogen adsorption isotherms.

in the range between 0.24 and 1.16 cc/g. For silicas of the specific surface area about 300 m^2/g or greater the total pore volumes are about 0.8-1.1 cc/g and the average pore widths are about 10 nm.

For remaining silicas, the total pore volumes are much lower and the average pore widths much higher. The average pore widths were calculated on the basis of the incremental pore volume distributions shown in Figures 3 and 4 and obtained by using the DFT software.[12]
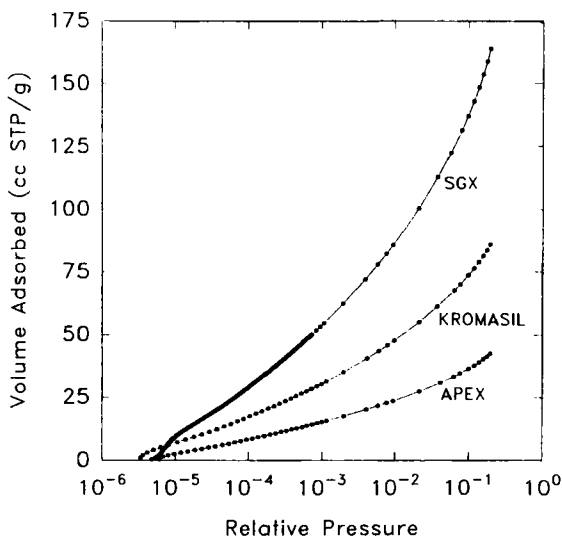
Figure 5. Low pressure nitrogen adsorption isotherms for Apex, Kromasil and SGX silica.

Table 1

Surface and Structural Parameters of the Chromatographic Silicas Studied

Silica	Source	$S_{BET}(m^2/g)$	$V_t(cc/g)$	w(nm)
Hypersil	Altech	56	0.24	52
Partisphere	Whatman	81	0.52	45
Vydac	Supelco	86	0.36	38
Apex	Jones Chrom.	153	0.57	15
Altima	Altech	294	0.86	12
Kromasil	Eka Nobel	311	0.85	11
Intersil	MetaChem Tech	357	1.16	16
SGX	Tesske	596	1.13	8

One can notice relatively narrow incremental pore volume distributions for Altima, Inertsil and Kromasil. Relatively broad pore volume distributions were obtained for Hypersil, Partisphere and Vydac. The pore volume distributions for Apex and SGX silicas are slightly broader than those for Altima, Inertsil and

Kromasil. Moreover, the pore volume distribution for the SGX silica shows a relatively high fraction of small pores and therefore its specific surface area is the highest among the samples studied.
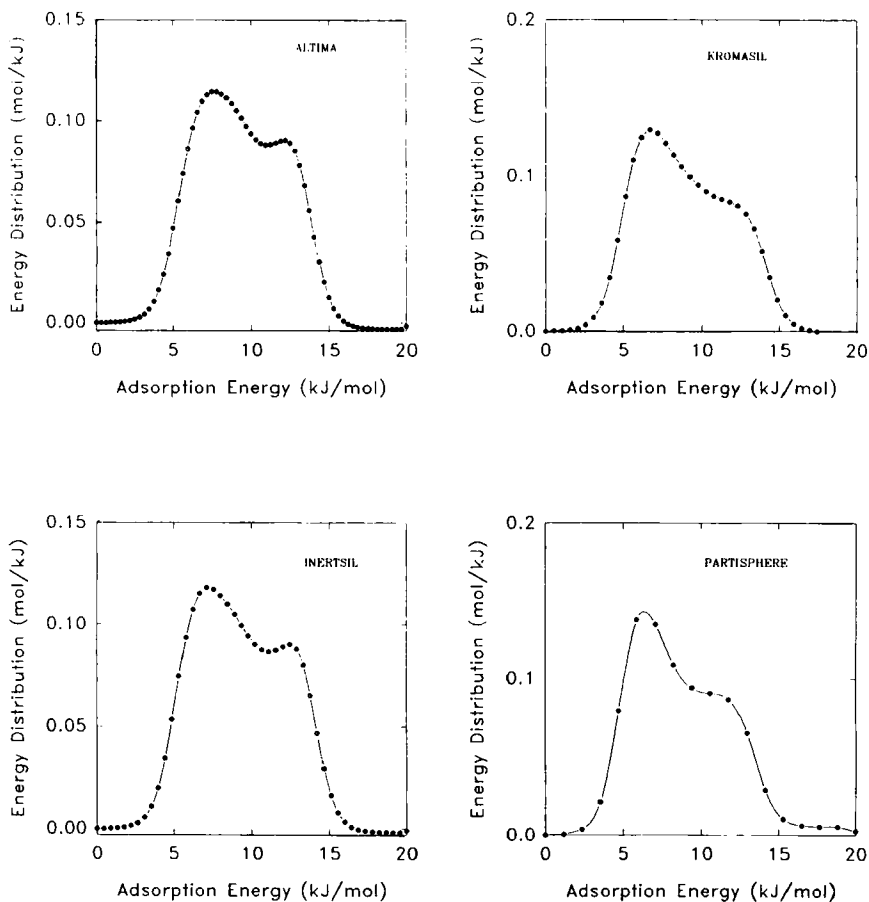
The adsorption energy distributions for all silica samples were calculated on the basis of data from the submonolayer range of nitrogen adsorption isotherms. An illustration of this range of adsorption data is shown in Figure 5, in which the volume adsorbed is plotted as a function of the logarithm of the relative pressure in order to demonstrate the differences between adsorption isotherms at the low pressure range.   Only experimental points below the relative pressure corresponding to the BET monolayer capacity were used to calculate the adsorption energy distributions according to Eq. 2.

The Fowler-Guggenheim model for a random distribution of adsorption sites was used to represent the local adsorption and gave much better results than the model for the patchwise distribution of adsorption sites.   The numerically stable energy distributions were obtained by assuming four nearest neighbors. The interaction parameter for nitrogen was equal to 95 K and the regularization parameter was equal to 0.1. The resulting adsorption energy distribution functions provide only approximate information about the energetic heterogeneity of the samples studied due to the simplicity of the FG model employed.

All energy distributions consist of at least two overlapping peaks with maxima located about 6 and 13 kJ/mol, respectively (see Figures 6 and 7). The appearance of two peaks in the energy distribution function suggests the presence of two main types of adsorption sites on the silica surface and agrees with previous studies.[7] For most silicas studied the upper adsorption energy is about 16-17 kJ/mol. Note that the energy distribution for the SGX silica does not exhibit two overlapping peaks of clearly pronounced maxima.

The small fraction of high energy sites can be noticed on the energy distributions for Partisphere, Vydac and Hypersil. For these silicas the energy distributions cover the range up to 20 kJ/mol.

The supplementary studies of the samples were performed by thermogravimetry[17] and showed that the three silicas mentioned above contain much more chemisorbed water than the remaining samples. Therefore, in order to estimate the impact of the surface water and silanols on the energetic heterogeneity of silicas further thermoanalytical and spectroscopic studies are desirable. These studies can provide valuable information about high-energy sites on the silica surface.

Figure 6. Adsorption energy distributions for Altima, Inertsil, Kromasil and Partisphere calculated from the low-pressure nitrogen adsorption data.

CONCLUSIONS

It is known that three major factors are responsible for the energetic heterogeneity of silicas: (i) different types of silanol groups present on the surface, (ii) impurities (usually metal oxides), and (iii) microporosity. For the silicas studied, except the SGX sample, the microporosity does not seem to play a significant role, so the remaining two factors account for their heterogeneity.
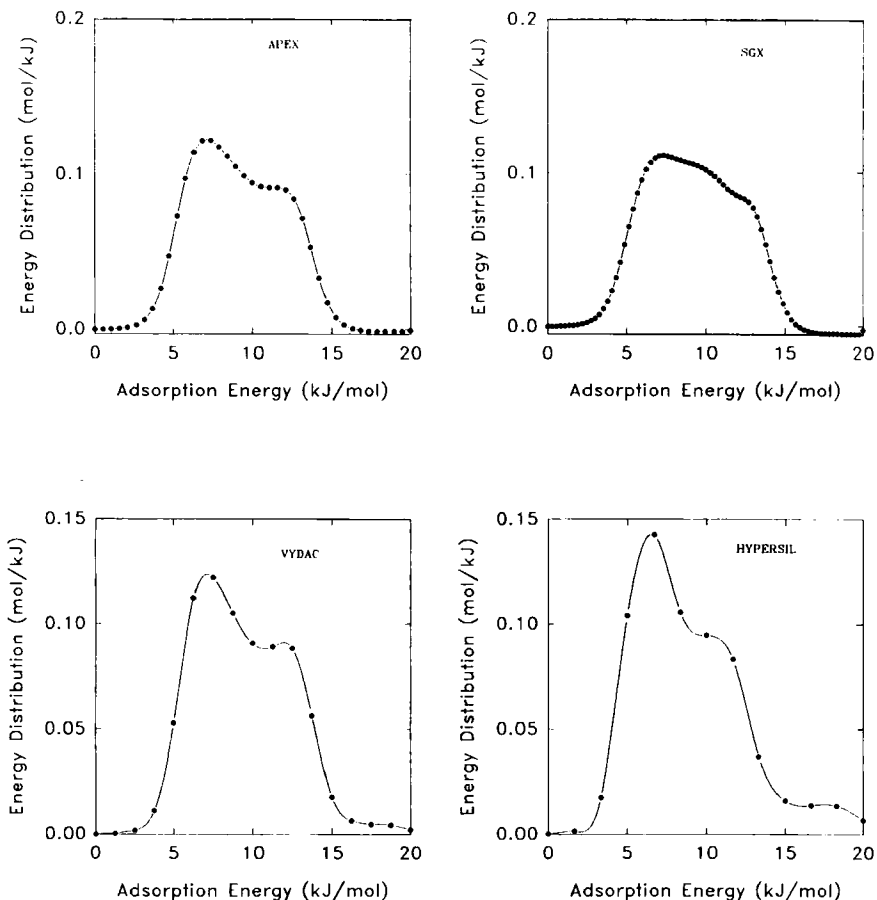
Figure 7. Adsorption energy distributions for Apex, SGX, Vydac and Hypersil calculated from the low-pressure nitrogen adsorption data.

Although the impurity level can be controlled, the silica surface possesses different types of silanol groups arranged in various topological patterns, which are an intrinsic feature of this surface and the primary source of its heterogeneity. It is shown, that adsorption methods allow for characterization of the energetic heterogeneity and provide information about porous structure of the samples, which are useful for optimization of the preparation conditions of chemically bonded stationary phases.

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