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Surface Textural Characteristics of the Prepared and Modified Silica Gel Surfaces

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Abstract
The objective of this study is to relate structural, textural and surface characteristics of silica gel surfaces to their various modifications. These modifications include calcination, hydrothermal treatment, coating and bonding with polyethylene glycol (Carbowax-20M) in addition to double modifications to obtain silica samples of different surface characteristics to cover many applications in different fields. Nitrogen adsorption was studied for monitoring the changes in textural properties of the parent and modified silica. The data indicates the widening in the pore accompanied the calcination and bonding with polymer. other aim of this work is of prime importance not only for understanding how modification is related to the changes in these properties but also to the change in the performance of these silica surfaces as adsorbents and chromatographic stationary phases. Surface chemistry and nitrogen adsorption must be taken into account in the decision-making process of choosing a selective adsorbent for each problem.

Keywords: structural, surface characteristics, calcination, hydrothermal treatment, coating and bonding.

INTRODUCTION

Silica gel is a common sorbent for stationary phase in chromatographic separations (Faramawy et al 1997, El-Fadly et al, 1997 and El-Naggar Turky, 2001), the structure of silica gel is a matrix of particles consists of silicon atoms joined together with oxygen atoms by siloxane bonds [Fig. (1-a)] (Silicon-oxygen-silicon bonds). On the surface of silica, some residual, uncondensed hydroxyl groups from the original polymeric silicic acid remain. These residual hydroxyl groups confer upon silica gel its polar properties. The silica surface is quite complex and contains more than one type of hydroxyl group, strongly bound or 'chemically' adsorbed water, loosely bound or 'physically adsorbed' water (Fig. 1-b) and hydrogen bonded silanol group (Fig. 1-c).

There are three types of hydroxyl group. The first is a single hydroxyl group attached to a silicon atom which has three siloxane bonds joining it to the gel matrix (Fig. 1-d). The second is one of two hydroxyl groups attached to the same silicon atom which, in turn, is joined to the matrix by only two siloxane bonds (Fig. 1-e). These twin hydroxyl groups are called Geminal hydroxyl groups. The third is one of three hydroxyl groups attached to a silicon atom which is now only joined to the silica matrix by only a single siloxane bond (Fig. 1-f**) (**Zhuravlev, 2000).

The chemical and adsorption properties of silica gel depend on number and reactivity of the surface silanol groups**.** Two forms of adsorption centers may exist over the surface of silica gel, 1) Hydroxyl group, 2) Coordinated unsaturated atoms of silicon and surfaced electronegativity atoms of oxygen nascent at dehydration of silica gel. The surface of dehydrated silica gel begins slightly to chemisorb oxygen, most likely on the centers of -Si type **(**El-Naggar et al 2013).

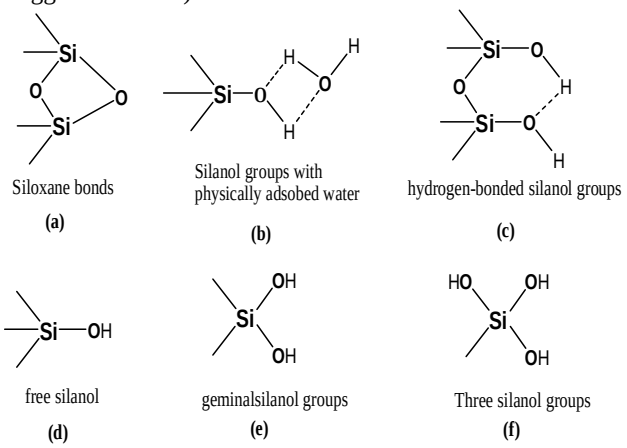

Figure (1): Different forms of hydroxyl group that can occur on the surface of silica gel.

In the present study silica gel was selected to investigate the influence of several surface modification and coating techniques on the surface textural characteristics of these materials compared with the parent silica gel. Also, the reflection of these changes on their uses as adsorbents and as solid stationary phases in gas chromatography.

EXPERIMENTAL

1. Preparation of Native Porous Silica

Porous silica was prepared from sodium meta silicate (Na_2SiO_3) from Avocado, Cat. No.10688 (England)

with SiO_2 content 45.8-47.3% by a conventional precipitation method according to de-Bore method (De Boer, 1971). Alumina was precipitated from a solution of 25 % wt/v $Al_2(SO_4)_3.18H_2O$ from Win lab, Cat. No.102183. Precipitation was made using ammonia solution of pH=12 and the precipitation pH were adjusted at 8.6. The dried silica and alumina samples was then crushed and sieved to 60-80 mesh, one batches were only used throughout this investigation.

MODIFICATION METHODS

Calcinations of native porous silica and alumina was take place in a muffle furnace at 1000°C for 5 hour to stabilize the number and type of active sites.

Parent silica samples were coated (El-Naggar and Turky, 2001). by loading 25wt% of the polyethyleneglycol stationary phase (Carbowax 20M) having high molecular weight), while calcined alumina (1000°C) were coated by loading 10wt%. The polymer was dissolved in a proper amount of chloroform and added to the sample. The mixture was heated in rotary evaporator till the complete evaporation of the chloroform. The coated sample was then dried at 120°C for 24hour.

Bonding by Polymer (Wray and Robert 1978)**.** was take place by transfer the above mentioned coated samples to a 50ml volumetric pipette containing a glass wool plug at the restricted end. The pipette was hold at a flow of nitrogen 200ml min^{-1} for at least 30min and reduced to 5ml min^{-1}. Then the temperature was raised to 270°C over a period of about 2h and maintained at that temperature for 20h before cooling to room temperature. The supports were then transferred to a soxhlet and successively extracted with dichloromethane and methanol for three weeks to remove all unbound polymer. The notations of the prepared samples are listed in Table (1).

Textural Analysis using N_2 Adsorption Technique (El-Fadly et al 1997)

The textural properties were determined from the N_2 adsorption-desorption isotherms measured at liquid nitrogen temperature (-196°C) using a Micromerities Genini III 2375 surface analyzer (Micromerities, Norcross, CA, USA). Perior to any adsorption measurement all samples were degassed at 473K under a reduced pressure of 10^{-4} Torr. The adsorption isotherm was constructed in term of the volume adsorbed (V cm^3g^{-1}) versus the equilibrium relative pressure P/P_o, where P is the equilibrium pressure and P_o is the saturated vapor pressure of nitrogen. After the completion of the adsorption isotherm, desorption was followed until the closure of the hysteresis loop

Table (1): Notation of the prepared samples

Notation	Treatments
Si	Parent silica gel (60-80 mesh)
Si_{C500}	Silica gel calcined at 500°C
Si_C	Silica gel calcined at 1000°C
Si_S	Silylated silica gel using dimethyldichlorosilane
Si_{CS}	Silylated calcined Silica gel
Si_{HT}	Hydrothermally treated silica gel
Si_{CHT}	Hydrothermally treated pre calcined silica gel
$Si_{Co25\%}$	Silica gel coating by 25% of polyethyleneglycol
$Si_{CCo10\%}$	Calcined silica gel coating by 10% of polyethyleneglycol
$Si_{Bo25\%}$	Silica gel bonding by 25% of polyethyleneglycol
$Si_{CBo10\%}$	Calcined silica gel bonding by 10% of polyethyleneglycol

RESULTS AND DISCUSSIONS

The textural properties of a solid are conventionally determined from the physical adsorption because this type of adsorption is not specific and thus determines the total surface area. Nitrogen is recommended to be the most suitable probe for surface area determination since it seldom goes into specific interaction with the solid surface (**Condon** , 2006). The N_2 adsorption-desorption isotherms of Si, Si_C, Si_{HT} and Si_{CHT} samples are shown in Fig. (2). Adsorption isotherm was constructed in term of the volume adsorbed (V cm^3g^{-1}) versus the equilibrium relative pressure P/P_o, where P is the equilibrium pressure and P_o is the saturated vapor pressure of nitrogen. All samples show type II isotherm according to IUPAC classification (Leofanti et al, 1998).

Three stages are shown by the nitrogen adsorption isotherms of Si, Si_C, Si_{HT} and Si_{CHT}. Two knee bends exist in each isotherm. The first knee is well developed and refers to the completion of monolayer and the beginning of multilayer adsorption. The second knee is broad and less developed, but is followed by a steep increase in the isotherm. This steep rise may be ascribed to capillary condensation in micropores. After the completion of the adsorption isotherm, desorption was followed until the closer of the hysteresis loop. Upon desorption pronounced hysteresis loop for Si (Fig. 2-a) was exhibiting H3 type which indicates the presence of micropores and/or mesopores of ink bottle shape (Lecloux and Pirard, 1997).

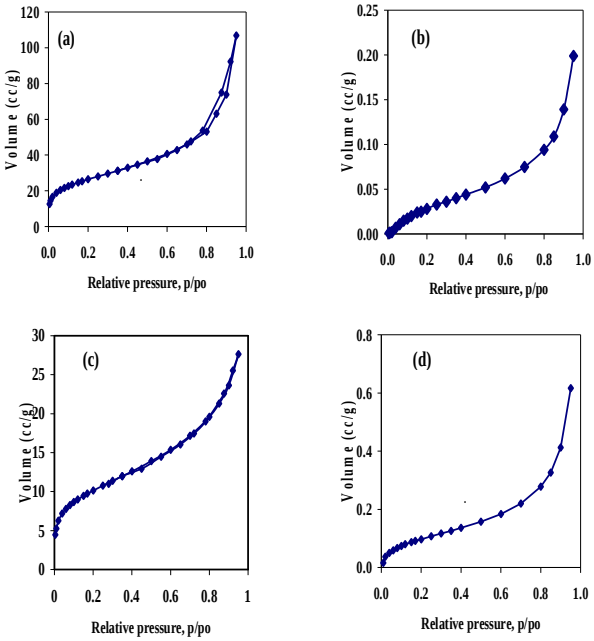

Figure (2):N_2 adsorption desorption isotherms of
a- Si b- Si_C
c- Si_{HT} d- Si_{CHT}

Si_C, Si_{HT} and Si_{CHT} sample isotherms (Fig. 2 (b-d)) are more or less reversible without hysteresis loop, i.e. desorption points lie on the same adsorption isotherm; this may indicate either the nonporous structure or the mesoporosity structure of the entire texture. The conventional BET equation was applied to analyze the adsorption isotherms of Si, Si_C, Si_{HT} and Si_{CHT}. The BET equation could be written in the linear form as:

$$P/P_o/ [V (1-P/P_o)] = 1/(V_m C) + [(C-1)/ (V_m C)] P/P_o \quad (1)$$

where, V (cm^3g^{-1}) is the adsorbed volume at pressure P and absolute temperature T, V_m (cm^3g^{-1}) is the volume of gas required to cover the whole surface of the solid with a unimolecular layer (the monolayer capacity) and C is a constant approximately equals to $e^{-(E1-EL)/RT}$ where E_1 is the heat of the adsorption of the first layer and E_L is the heat of condensation of the nitrogen gas to a liquid.

The specific surface area was evaluated by the BET equation in its normal range of applicability. The plot of $P/P_o/ [V (1-P/P_o)]$ vs. P/P_o yields a straight line within the range P/P_o = 0.05-0.35. The slope of this straight line equals $(C-1)/ CV_m$ and its intercept equal $1/CV_m$. The values of V_m and C could therefore be calculated. The surface area, (S_{BET}) is estimated using the following relationship:

$$S_{BET} (cm^2g^{-1}) = (V_m. N. A_m. 10^{-20}) / 22414 \quad (2)$$

Where, N is Avogadro's number and A_m is the molecular cross sectional area of nitrogen taken as 16.2Å^2 (Young and Crowell, 1962).

The total pore volume could be calculated from the amount adsorbed at saturation pressure i.e, $P/P_o \sim 1$ using the relationship:

$$V_p = V_{st} X (MV_{sp} /M_v) \quad (3)$$

where, V_p is the volume of nitrogen in the form of liquid per one gram solid, adsorbed at the saturated vapor pressure, i.e. $P/P_o \sim 1$, M is the molecular weight of nitrogen (28.016), M_v is the molecular volume of nitrogen and V_{sp} is specific volume of nitrogen (1.238 $cm^3 g^{-1}$).

$$V_p = 1.55 \times 10^{-4} V_{st} \quad (4)$$

The linear BET plots are shown in Fig. 2(a-d). The adsorption data fits well the BET equation as indicated by the absence of any scatter of data point away from the linear BET plots.

The surface areas as determined from the BET equation (S_{BET}, m^2/g) are given in column (3) of Table (2). Column (2) of this table shows the value of the BET-C constant, (i.e. C_{BET}). The total pore volume V_P (ml/g) was calculated by converting the volume of nitrogen gas adsorbed at $p/p_o \approx 1.0$ to the volume of nitrogen as a liquid. V_P values are given in column (5) of Table (2). The average pore radius was calculated and listed in column (6) of Table (2) using the relationship (5).

$$r_a (nm) = (2 \times V_p \times 10^3)/S_{BET} \quad (5)$$

Inspection of Table (2) reveals that:

(i) Calcinations of Si at 1000^{o}C is associated with a drastic decrease in the surface, total pore volume but with a tremendous increase in pore radius

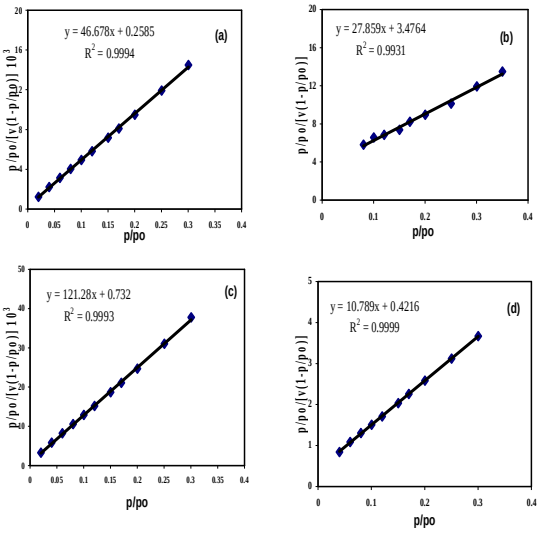

Figure (3): BET relation ship
a- Si b- Si_C
c- Si_{HT} d- Si_{CHT}

Table 2: Textural properties of parent and modified silica samples

Sample	C_{BET}	S_{BET}, m^2/g	S_t, m^2/g	
Si	182	93.1	95.37	
Si_C	9.02	<1	<1	
Si_{HT}	167	35.8	36.599	
Si_{CHT}	27.66	<1	<1	

(ii) The textural properties of Si_C discussed in this section are also related to the crystallization of silica into crystoballite and tridymite. Crystalline solids are characterized by their low surface area and porosity. This may be taken as evidence that for the sensitivity of textural properties are to structural changes and phase transition.

(iii) The textural parameters of Si_{HT} are lower than those determined for the parent silica Si, thus S_{BET} of Si_{HT} is 35.8 m^2/g only about 40% of the S_{BET} determined for Si, more than 65% decrease in total pore volume and consequently about 25% decrease in r_a. However, the values of the textural parameters of Si_{HT} are by far higher than those measured for Si_{CHT}.

(iv) Low surface area and porosity of both Si_C and Si_{CHT} makes the conclusion in this respect unreasonable.

Surface area and porosity were also detected from a plot of gas adsorbed (v) against film thickness (t). The v-t plot is an independent method that has been used to determine the surface area S_t. This method implies the consideration of a standard t-curve which is a plot of the statistical thickness t of the adsorbed film against p/p_o for a nonporous adsorbent. Successful determination of S_t is obtained if the appropriate t-curve is selected. The selection is based on the value of C_{BET}. The plot should be a straight line passed through the origin and specific surface area may be obtained from the slope using equation:

$$\mathbf{S_t = 1.547\ (V/\ t)} \qquad \mathbf{(6)}$$

With V in $cm^3\ g^{-1}$, t in nm and S_t in $m^2\ g^{-1}$

The t-curve of Sing and Ryne (Sing and Ryne, 1996). was used, in the present investigation. Figure (4) evidently the v-t curve of Si although looks linear, it shows small downward and upward deviation indicating thus the existence of both micro and mesoporosity. The v-t plot of Si_{HT} (Fig. 3) may be taken as an evidence for the mesoporous texture of this sample. On the other hand the v-t plot of Si_C and Si_{CHT} are typical straight line indicating non-porous structure with the possible existence of a small fraction of mesoporosity. This indicates that hydrothermal treatment of Si_C is not associated by any pronounced change in the textural.

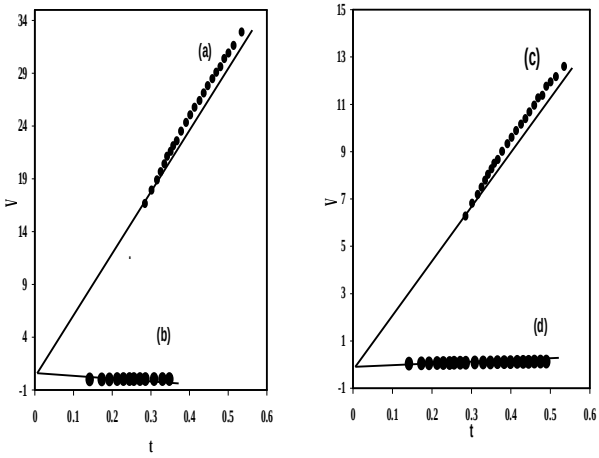

Figure (4): V-t plot of:
a- Si b- Si_C
c- Si_{HT} d- Si_{CHT}

The S_t values were calculated from the slope of the linear part of the v-t plots and are listed in column 4 of Table (2).

(i) The v-t plot of Si_C suggests the high possibility of a non-porous structure.

(ii) The agreement between S_{BET} and S_t values suggests that these two methods could be considered complementary and indicate in the same time the correct choice of the standard t-curve.

The pore size distribution and shape are closely related to the hysteresis loop classified by IUPAC, BET or BDDT. The porosity was detected by applying BJH method (Barrett et al, 1951). Pore size distribution curve was constructed by plotting pore radius, r_p in nm against dV/dr_p, which is the first differentiation between pore volume and pore radius at different relative pressure (P/P_o).

$$\mathbf{r_p = (4.15/\log P/P_o)\ x10^{-10}} \qquad \mathbf{(7)}$$

The pore size distribution curve of parent silica Si is shown in Fig. (5). The distribution curve depicts the existence of a very small fraction of micropores with r < 2.0 nm, a large fraction of mesoporosity exists and their percentages decrease with the increase of r within the mesoporosity range. It seems from these distribution curves that wide pores represent a small fraction of the total porosity. The pore size distribution curve for Si_{HT} is shown in Fig. (5-b). The curve is multi-model exhibiting three maxima at r values of 1.6, 2.1 and 3.2nm and a broad maximum at r = 6-12nm. These maxima and the distribution curve as a whole describe mesoporous solid.

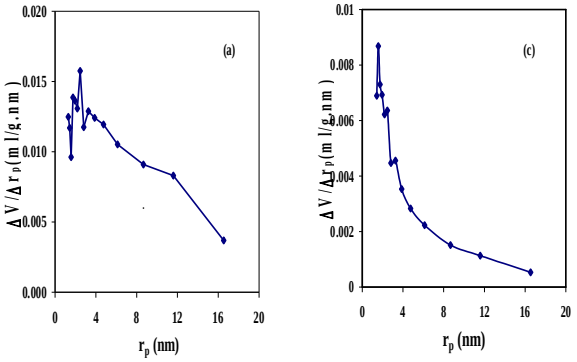

Figure (5): PSD curves for a- Si & b-Si_{HT}.

Figure (6) shows the nitrogen adsorption-desorption isotherms of Si_S, Si_{CS}, $Si_{Co25\%}$ and $Si_{CBo10\%}$. The Si_S sample has type II isotherm with a shift to lower partial pressure of the capillary condensation as compared with Si. While the isotherms of the other three samples are typical type II with no hysteresis, i.e. desorption point lies on the same adsorption isotherm.

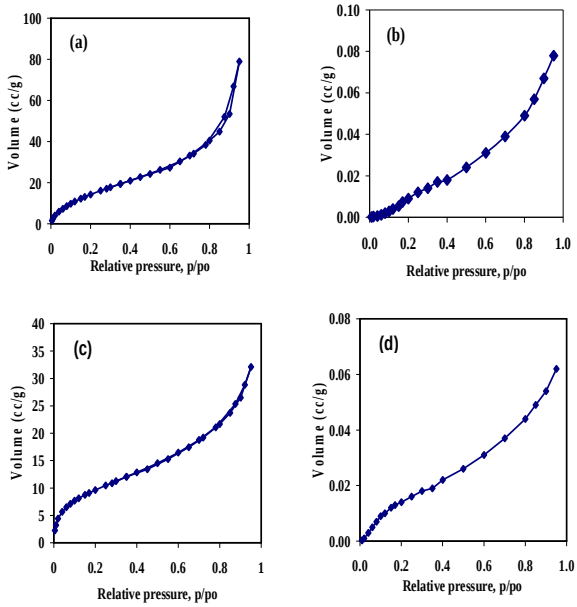

Figure (6):N_2 adsorption desorption isotherms of
a- Si_S b- Si_{CS} c- $Si_{Co25\%}$ d-$Si_{Cbo10\%}$

Figure (7) shows the linear BET plots of Si_S, Si_{CS}, $Si_{Co25\%}$ and $Si_{CBo10\%}$. Satisfactory linear plot is shown for Si_{CS} whereas excellent fit for the BET equation was observed for Si_S, $Si_{Co25\%}$ and $Si_{CBo10\%}$ as indicated by the absence of any scatter of data point away from the linear BET plots. Table (3) lists the textural properties of Si_S, Si_{CS}, $Si_{Co25\%}$ and $Si_{CBo10\%}$. This table revels that silylation of parent silica is associated with about 40% decrease in the surface area, 35% decrease in the total pore volume but with about 10% increase in the average pore radius. The drastic decreases in the value of C_{BET} constant refer to the lowering in the heat of adsorption in initial portion of the adsorption isotherm. Coating of parent silica is also associated with a considerable decrease in the value of the C_{BET} constant describing the heat of adsorption in the first layer.

The decrease of surface area due to polymer coating of silica ($Si_{Co25\%}$) amounts to about 61% and the decrease in the value of V_p amounts to ≈ 74%. Coating of Si with polymer was also associated with about 30% decrease in the average pore radius. The decrease of surface area due to polymer coating of silica ($Si_{Co25\%}$) amounts to about 61% and the decrease in the value of V_p amounts to ≈ 74%.

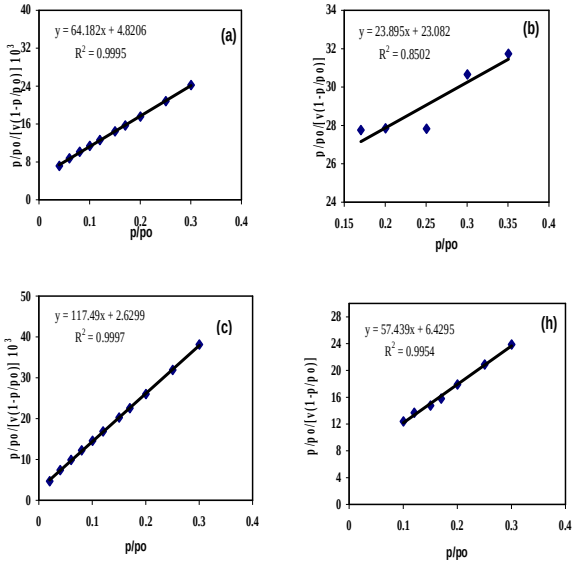

Figure (7): BET relation ship
a- Si_S b- Si_{CS}
c- $Si_{Co25\%}$ d-$Si_{CBo10\%}$

Coating of Si with polymer was also associated with about 30% decrease in the average pore radius. Polymer molecules may be accessible to relatively wide pores and the precipitation in these pores may account for this pore narrowing. Calcination followed by silylation is also found to be associated with a decrease in surface area. The values presented for the textural parameters for Si_{CS} and $Si_{CBo10\%}$ are too low to account for. This is not surprising to the author because calcinations at temperature as high as 1000°C not only changes the textural properties but also the structural properties. It has already been mentioned in this thesis that calcinations of Si at 1000°C are associated with phase changes including amorphous to crystalline transition.

Table (3): Textural properties of parent and modified silica samples

Sample	C_{BET}	S_{BET}, m^2/g	S_t, m^2/g	V_p, ml/g	r_a, nm
Si_S	14.3	63.3	57.04	0.122	3.855
Si_{CS}	2.036	<1	<1	-	-
$Si_{Co25\%}$	46	36.4	36.38	0.0497	2.731
$Si_{CBo10\%}$	9.95	<1	<1	-	-

The v-t plots of Si_S, Si_{CS}, $Si_{Co25\%}$ and $Si_{CBo10\%}$ are shown in Fig. (8). This figure shows that, v-t of Si_S shows upward deviation which indicates the mesopores structure of this sample. For Si_{CS}, $Si_{Co25\%}$ and $Si_{CBo10\%}$ a slight downward deviation at small t-values is observed in their v-t plots and also an upward deviation at high t-values is observed. It seems that, modification with polymer and silylation can cause some change in the texture of Si and Si_C.

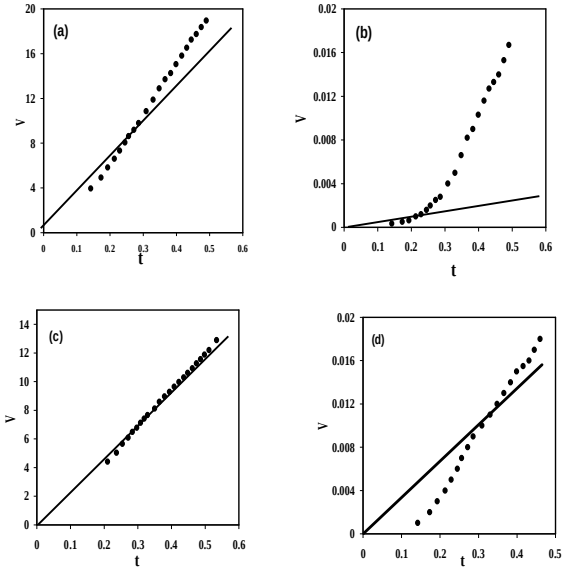

Figure (8): V-t plot of: a- Si_S b- Si_{CS} c- $Si_{Co25\%}$ d- $Si_{CBo10\%}$

Figure (9) shows the pore size distribution of Si, $Si_{Co25\%}$ and Si_S. Surface coating with polymers increased the percentage of micropores whereas the size of mesopores decreased. Coating is probably associated with partial closure of wide pores, decreasing their percentage and meanwhile increases the percentage of micropore. On the other hand, Si_S exhibits multi-modal pore size distribution, the highest maximum is located at ≈ 2nm and two short maxima were exhibited at ≈ 4.8 and 11.6 nm.

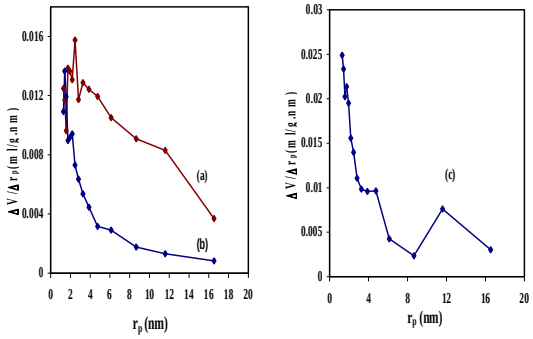

Figure (9): PSD curves of a- Si b- $Si_{Co25\%}$ c- Si_S

CONCLUSION

The textural properties comprise the surface area, total pore volume, mean pore radius and pore size distribution, are very sensitive to thermal treatment. All treatment of silica samples brought a decrease in these textural properties. Calcination and hydrothermal treatment were associated with a very drastic decrease in the surface area and total pore volume and with pore widening with respect to the parent one. However, coating of silica with polymer caused considerable decrease both in the total pore volume and the average pore radius referring thus to complete or partial closure of the silica pores.

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