

Preparation, Silylation and Coating of SiO₂ in relation to their surface characteristics

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Abstract

Preparation and both silylation and polymer coating of silica were prepared and selected to investigate their influence on the surface textural characteristics of silica compared with their untreated surfaces. Silylation and coating of silica were achieved using dimethyldi chlorosilane and Polyethylene glycol respectively. Polymer coated materials are associated by a pronounced decrease in surface area, total pore volume and pore radii comparing with the uncoated materials. The Silylated silica has type II isotherm with a shift to lower partial pressure of the capillary condensation while the isotherms of the coated samples are typical type II with no hysteresis. Coating is probably associated with partial closure of wide pores and meanwhile increases the percentage of micro pore. On the other hand, SiS exhibits multi-modal pore size distribution.

Key words: Preparation, Silylation, polymer coating, Surface textural characteristics, , pore size distribution.

Introduction

Silica is a common sorbent in chromatographic separations [1-3], The physical and chemical properties of silica depends on number and reactivity of their surfaces. The effect of polymer coating on the pore structure properties of silica was studied with nitrogen adsorption [4]. 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. Therefore, the surface chemistry of alumina is complex, alumina surfaces are high active towards adsorption when compared to silica and the number of active adsorption sites on alumina can be around 100 times higher than those on silica [5]. This complexity is illustrated by comparing the results of various characterization methods on alumina and silica.

In the present study silica was selected to investigate the influence of coating techniques on the surface textural characteristics of this material compared with the parent silica.

Experimental

1. Preparation of 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 [6]. Alumina was precipitated from a solution of 25 % wt/v $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ 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.

2- Calcination [7]

Silica and alumina samples were calcined in a muffle furnace at 500°C for 16hr and at 1000°C for 5h to stabilize the number and type of active sites.

3- Silylation using dimethyldichlorosilane [8]

The method used for preparing the silylating samples was the same as that described earlier by; the sample was refluxed in a soxhelet by 30vol% of dimethyldichlorosilane in toluene for 6h. Then, the sample was removed from the soxhelet, washed by deionized water, and dried at 120°C overnight.

4. Coating methods

Parent silica and alumina samples were coated [9]. by loading 25wt% of the polyethyleneglycol stationary phase (Carbowax 20M) having high molecular weight), while calcined alumina (1000°C) were coated by loading 10 wt%. 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 [10] 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).

3. Textural analysis using N₂ adsorption technique [11]

The textural properties were determined from the N₂ adsorption-desorption isotherms measured at liquid nitrogen temperature (-196°C) using a Micromeritics Genini III 2375 surface analyzer (Micromeritics, Norcross, CA, USA). Prior 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 ($V \text{ cm}^3\text{g}^{-1}$) 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. The notations of the prepared samples are listed in Table (1).

Table (1): Notation of the silylated and coated silica samples.

Notation	Treatments
Si	Parent silica gel (60-80 mesh)
Si_s	Silylated silica gel using dimethyldichlorosilane
Si_{CS}	Silylated calcined Silica gel
Si_{Co25%}	Silica gel coating by 25% of polyethyleneglycol
Si_{Bo25%}	Silica gel bonding by 25% of polyethyleneglycol

The textural properties of studied solid samples 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 [12]. Adsorption isotherm was constructed in term of the volume adsorbed ($V \text{ cm}^3\text{g}^{-1}$) 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 [13].

Figure (1) shows the nitrogen adsorption-desorption isotherms of Si_s, Si_{CS}, Si_{Co25%} and Si_{CB010%}. 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 coated polymer samples are typical type II with no hysteresis, i.e. desorption point lies on the same adsorption isotherm.

Figure (2) shows the linear BET plots of Si_S , Si_CS , $\text{Si}_\text{Co25\%}$ and $\text{Si}_\text{CBo10\%}$. Satisfactory linear plot is shown for Si_CS whereas excellent fit for the BET equation was observed for Si_S , $\text{Si}_\text{Co25\%}$ and $\text{Si}_\text{CBo10\%}$ as indicated by the absence of any scatter of data point away from the linear BET plots. Table (2) lists the textural properties of Si_S , Si_CS , $\text{Si}_\text{Co25\%}$ and $\text{Si}_\text{CBo10\%}$. This table reveals 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 ($\text{Si}_\text{Co25\%}$) amounts to about 61% and the decrease in the value of V_p amounts to $\approx 74\%$. 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 [14]. 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 $\text{Si}_\text{CBo10\%}$ are too low to account for.

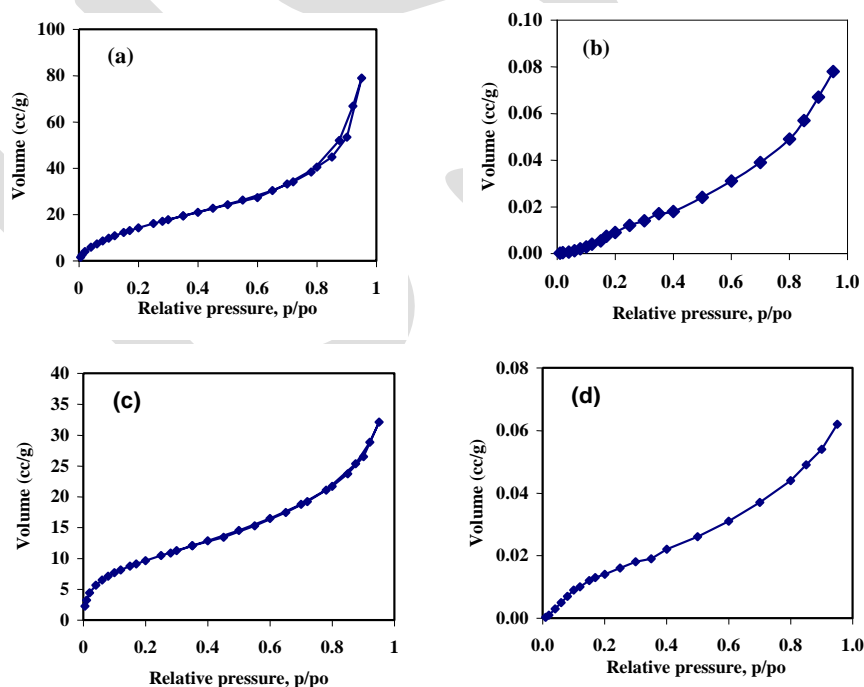


Figure (1): N_2 adsorption desorption isotherms of a- Si_S b- Si_CS
c- $\text{Si}_\text{Co25\%}$ d- $\text{Si}_\text{CBo10\%}$

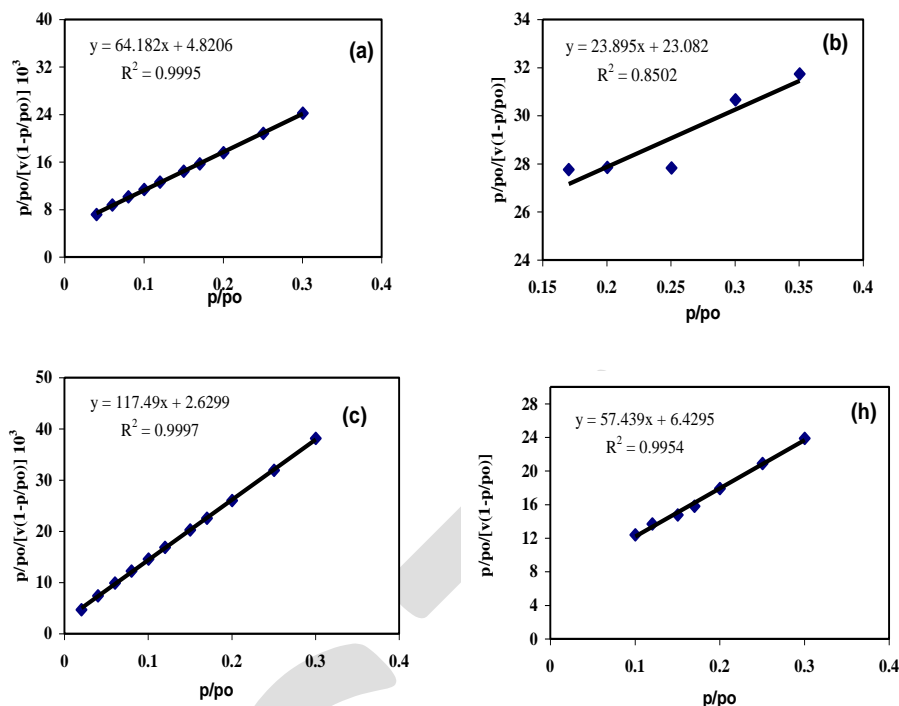


Figure (2): BET relation ship a- Si_S b- Si_{CS} c- Si_{Co25%} d-Si_{CB010%}

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 that calcinations of Si at 1000°C are associated with phase changes including amorphous to crystalline transition.

Table (2): 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 _{CB010%}	9.95	<1	<1	-	-

The v-t plots of Si_S, Si_{CS}, Si_{Co25%} and Si_{CB010%} are shown in Fig. (3), v-t of Si_S shows upward deviation which indicates the mesopores structure of this sample. For Si_{CS}, Si_{Co25%} and Si_{CB010%} 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 (4) 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 ≈ 2 nm and two short maxima were exhibited at ≈ 4.8 and 11.6nm.

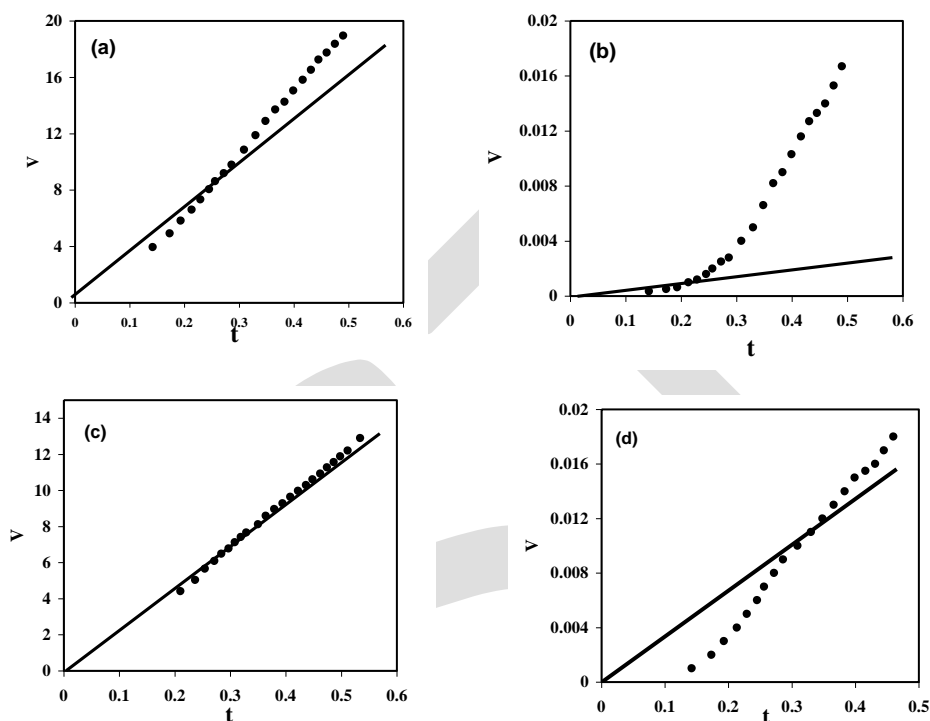


Figure (3): V-t plot of a- Si_S b- Si_{CS} c- Si_{Co25%} d- Si_{CB010%}

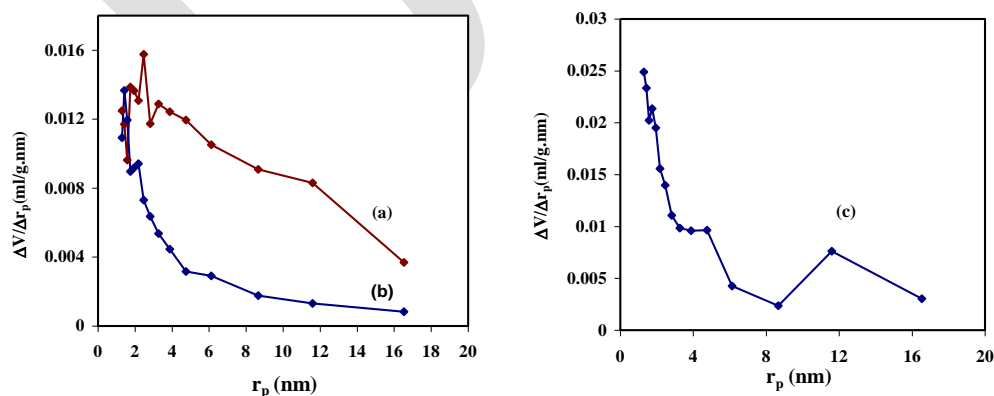


Figure (4): PSD curves of a- Si b- Si_{Co25%} c- Si_S

Conclusion

- Silylation of calcined silica was 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.
- 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 coated samples are typical type II with no hysteresis, i.e. desorption point lies on the same adsorption isotherm.
- Calcinations of Si at 1000°C are associated with phase changes including amorphous to crystalline transition, calcination followed by silylation was associated with a decrease in surface area.
- 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 $\approx 2\text{nm}$ and two short maxima were exhibited at ≈ 4.8 and 11.6nm .

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