The influence of synthesis conditions, oligosaccharide additive and functional silane on the structure and composition of sol-gel silicas

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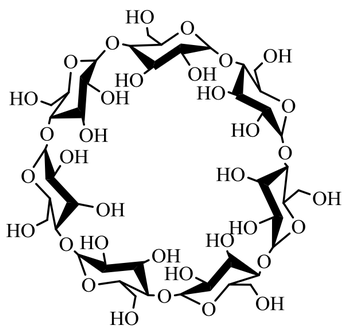
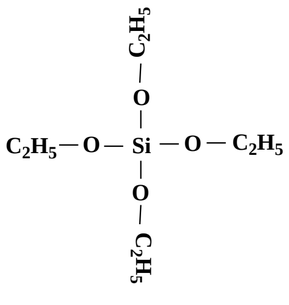
Sol-gel method is effective procedure to modify the surface of materials. Characteristics of silica materials obtained by sol-gel method depend on the experimental conditions applied (composition of the initial feedstock, variations in temperature, time, and type of treatment (like hydrothermal or microwave)). It is possible to obtain silicas with desirable structural characteristic (surface area, pore diameter, ordered or disordered pores) as well as solids with improved surface properties, which makes them widely used materials in separation, catalysis and drug delivery processes.

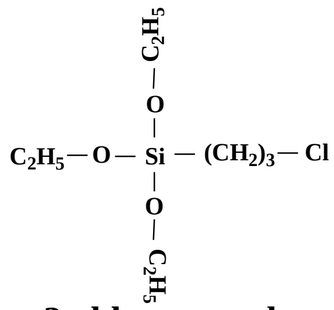
In this work, the influence of different experimental conditions on the structure and composition of silicas was elucidated. Gas phase adsorption and liquid sorption experiments were carried out to study the role of silica structure and composition on aromatic compounds' uptake.



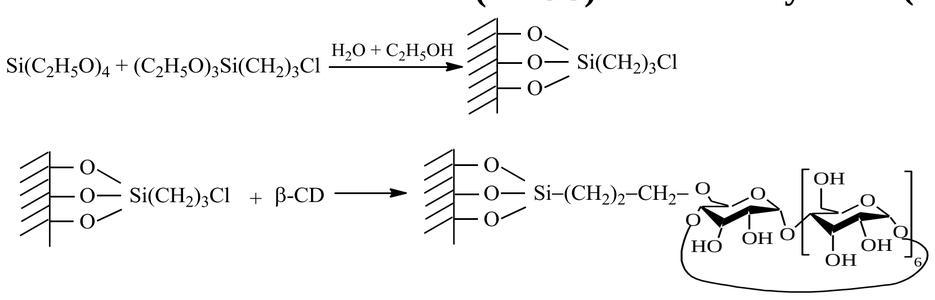
β-cyclodextrin



tetraethoxy silane (TEOS)

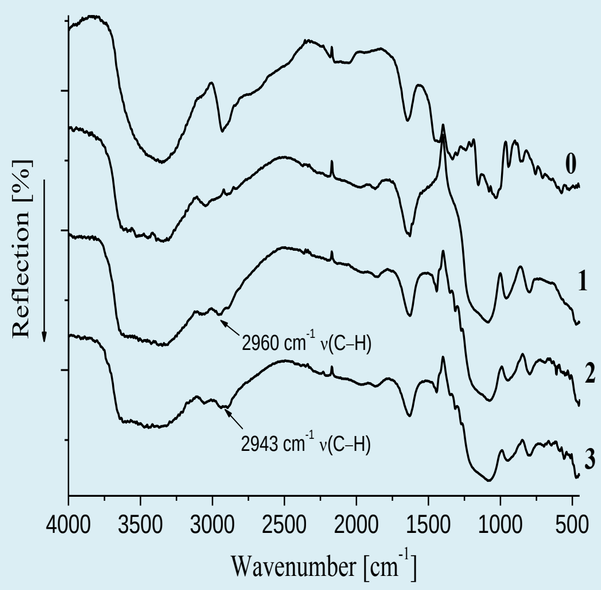


3-chloropropyl-triethoxysilane (CPTEOS)

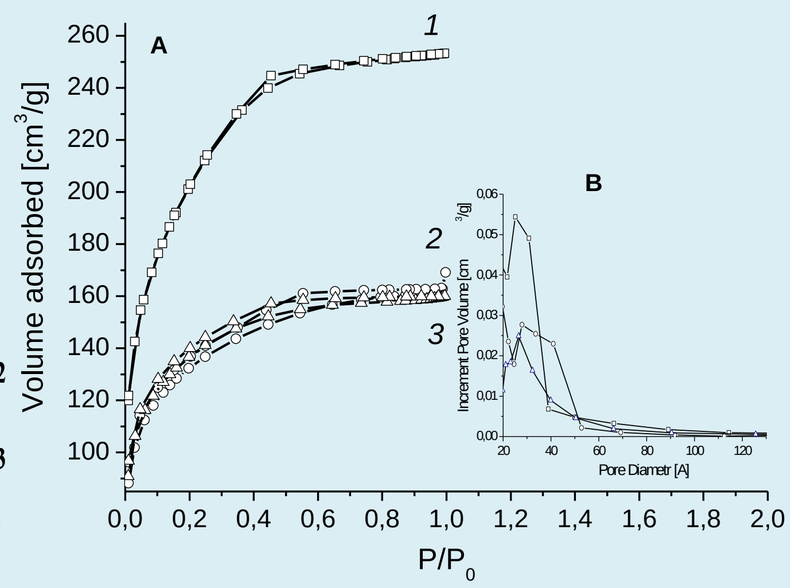


Silica material	TEOS/ CPTEOS molar ratio	Synthesis conditions	S_{BET}, [m^2/g]	V_{micro}, [cm^3/g]	V_{meso}, [cm^3/g]	CD content, [μmol/g]
TEOS	–	70 °C	863	0.033	0.291	–
TEOS	–	150 °C, 3h	720	0.044	0.206	–
TEOS/CPTEOS	8 : 1	70 °C	530	0.129	0.198	–
TEOS/CPTEOS	8 : 1	150 °C, 3h	489	0.124	0.188	–
TEOS/CPTEOS	5 : 1	70 °C	396	0.084	0.171	–
TEOS/CPTEOS	5 : 1	150 °C, 3h	470	0.081	0.155	–
TEOS/CPTEOS/ β-CD	8 : 1	70 °C	533	0.129	0.202	3.54
TEOS/CPTEOS/ β-CD	8 : 1	150 °C, 3h	577	0.131	0.131	2.76
TEOS/CPTEOS/ β-CD	5 : 1	70 °C	429	0.107	0.177	4.83
TEOS/CPTEOS/ β-CD	5 : 1	150 °C, 3h	485	0.083	0.134	2.66

Characterization



DRIFT spectra of synthesized silicas



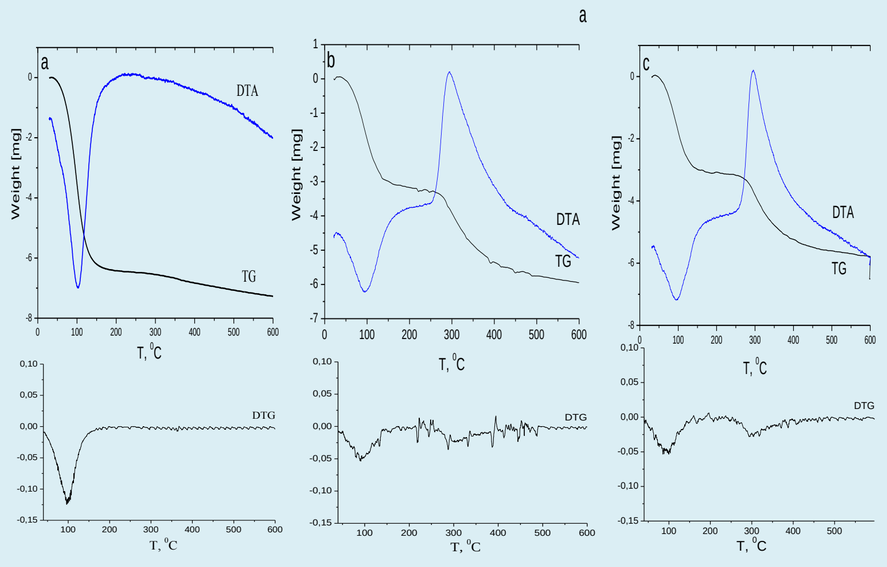
N_2 adsorption-desorption isotherms (A) and pore size distribution (B) for synthesized silicas

3320 см$^{-1}$ ν(O–H) (β-CD)
2930 см$^{-1}$ ν(C–H) (β-CD)
1640 см$^{-1}$ δ(O–H) (β-CD)

1100 см$^{-1}$ ν(Si–O–Si)
960 см$^{-1}$ ν(Si–O(H))

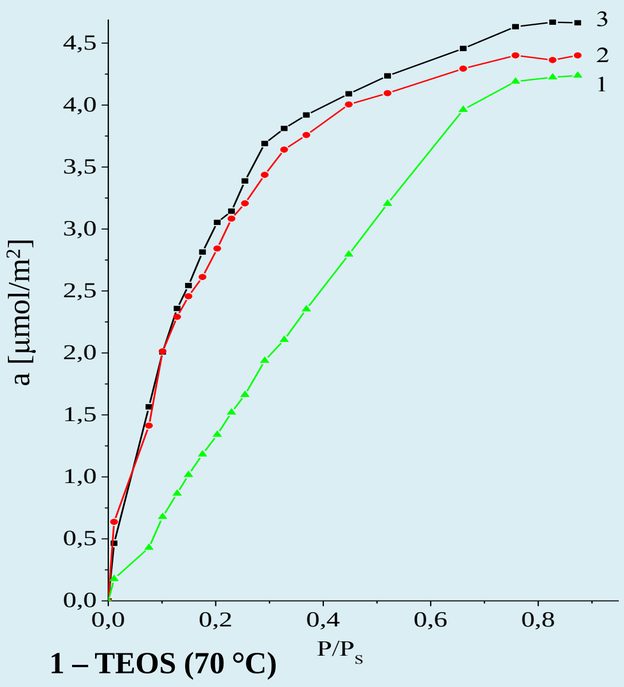
2960 см$^{-1}$ ν(C–H) (SiO_2–CPTEOS)
2943 см$^{-1}$ ν(C–H) (SiO_2–β-CD)
1443см$^{-1}$ δ(C–H)
1400–1200 см$^{-1}$ ν(C–O) та δ(C–H)
1200–900 см$^{-1}$ ν(C–OH) та ν(C–O–C)

0 – β-CD
1 – TEOS (70 °C)
2 – TEOS/CPTEOS (5:1) ((70 °C)
3 – TEOS/CPTEOS/β-CD (5:1) (70 °C)



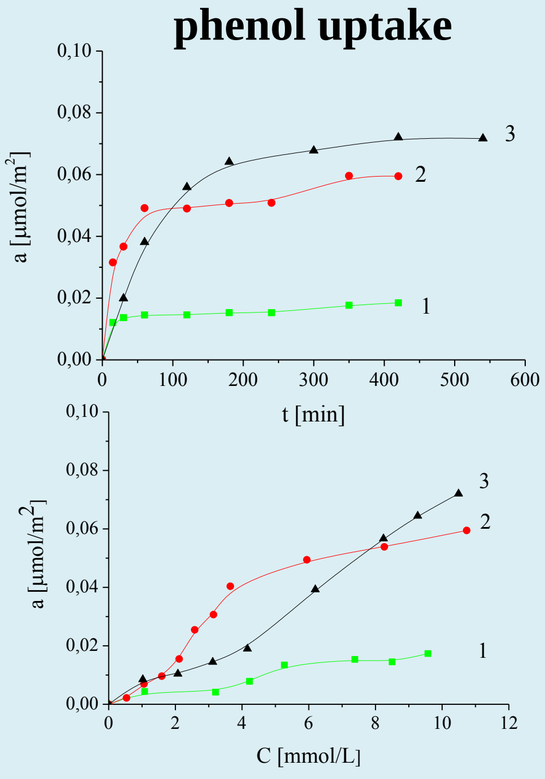
Thermal analysis of TEOS (a), TEOS/CPTEOS (b), and TEOS/CPTEOS/β-CD (c) silicas

Gas phase benzene adsorption



1 – TEOS (70 °C)
2 – TEOS/CPTEOS (5:1) ((70 °C)
3 – TEOS/CPTEOS/β-CD (5:1) ((70 °C)

Liquid sorption experiments on phenol uptake



Conclusions

Hydrolytically unstable Si–O–C linkages are formed as a result of sol-gel synthesis of CD-containing silicas from TEOS and CD.

Hydrolytically stable CD-containing silicas were prepared by hydrolysis and polycondensation of TEOS and CPTEOS, where the stronger C–O–C linkages are formed.

The band assignments of DRIFT spectra confirm the presence of organic moieties in functionalized silicas.

The porosity analysis demonstrates that silica materials are an isotherm Type I substance and pore size distributions with maximum at 2–5 nm. The surface areas of organosilicas are of more than 400 m^2/g.

Thermogravimetric analysis of functional silicas reveals an important weight loss in the temperature range 235–480 °C, corresponding to the progressive decomposition of the organic moieties.

Sol-gel synthesis of silicas with incorporated oligosaccharide and chloropropyl moieties can therefore be considered for the preparation of sorbents for effective separation and removal of aromatic compounds from aqueous media.