



Synthesis and CO₂ sorption of silica particles, kinetics and thermodynamics

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ABSTRACT

Spherical ordered mesoporous silica particles with radially oriented mesopores were successfully prepared by using non-ionic amphiphilic di-block co-polymers C_nH_{2n+1}-(EO)_x-OH as template and tetraorthosilicate (TEOS) as silica precursor. The synthesized mesoporous silica materials were characterized by XRD, N₂ adsorption-desorption and SEM techniques. CO₂ adsorption at 0 °C was evaluated by a volumetric method, and the CO₂ sorption behavior was described by applying both Langmuir and Freundlich equations. Results indicate a high adsorption capacity of CO₂ (5-9 mmol/g), depending essentially on the porous texture of the materials. An adsorption kinetic model was proposed to describe the adsorption of CO₂ over template-free mesoporous siliceous materials. A good agreement with experimental data was found.

Keywords: Non-ionic surfactants; Mesoporous silica; CO₂ adsorption; Langmuir and Freundlich models, Kinetics models.

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INTRODUCTION

Discovered in the early 90's (Kresge et al., 1992; Beck et al., 1992), ordered mesoporous materials are usually obtained in the presence of surfactants which act as organic structuring agents and molecular inorganic precursors. The interaction between organic and inorganic counter parts leads to the formation of ordered hybrid mesophases. Among the ordered mesoporous siliceous materials, there are those that are obtained from non-ionic surfactants such as tri-block copolymers $(EO)_x(PO)_y(EO)_x$ (SBA-15 and SBA-16) (Zhao et al., 1998; Sakamoto et al., 2000) and di-block copolymers $C_nH_{2n+1}(EO)_x$ named MSU-X (Ryoo et al., 1997; Bagshaw et al., 1995; Huo et al., 1995; Richer and Mercier, 2001), and whose pore size can reach 10 nm and wall thickness of about 3 nm.

Usually, it is assumed that the solubilization of such surfactants in aqueous medium is due to the association of water molecules with ethylene oxide groups by hydrogen bonds. Moreover in an acidic medium, the hydronium ion can be easily associated to the oxygen atom of the oxyethylene group, thus developing electrostatic interactions. Kim *et al.* (2002) showed that there is a correlation between the size of the hydrophilic and hydrophobic segments in non-ionic surfactants and the pore mesostructure of the solid after synthesis; the amphiphilic di-block copolymers C_nEO_x (with $C = C_nH_{2n+1}$ and $EO = -CH_2CH_2O-$) lead to an arrangement of pores that depends on the ratio volume of hydrophilic portion V_H to volume of hydrophobic portion V_L . For example, the use of surfactants $C_{16}EO_x$ leads to lamellar ($x=6$), 2-d slightly distorted hexagonal, disordered ($x=10$), and cubic ($x=20$) mesostructures.

Ordered mesoporous silica have appeared to be good adsorbent for CO_2 due to their high specific surface area, high pore volume and pore sizes between the upper limit of zeolites and the lower end of the mesoporous materials (Macario et al., 2005). In recent years, research activities have been focused on the study of CO_2 adsorption onto zeolites (Cavenati et al., 2004), activated carbon (Himeni et al., 2005), metal-organic frameworks (Caskey et al., 2008), amine-modified materials [Sanz et al., 2010; Yan et al., 2011; Heydari-Gorgi and Sayari, 2011] and membranes (Chew et al., 2010). More recently, Hao *et al.* (2010) prepared spherical silica with centered mesopores, and suggested that the prepared materials could be suitable for adsorption-based separations, because all the mesopores in the materials were connected to each other, leading to better adsorption properties. However, no investigation was realized to study the potential of synthesized materials as sorbents.

In the present work, a set of spherical ordered mesoporous silica materials have been synthesized with Di-block type copolymers $C_nH_{2n+1}(EO)_x$ as templating agents. In view of a possible use of these solids for CO_2 removal, their adsorption-desorption properties towards CO_2 were investigated at $0^\circ C$.

EXPERIMENTAL

Chemicals

Polyoxyethylene (20) oleyl ether ($C_{18}EO_{20}$) Brij®98, polyoxyethylene (20) stearyl ether ($C_{18}EO_{20}$) Brij®78 and polyoxyethylene (23) lauryl ether ($C_{12}EO_{23}$) Brij®35 surfactants have been provided by ACROS Organics Inc. Polyoxyethylene (40) nonylphenyl ether, branched ($C_{15}EO_{40}$) IGEPAL®CO-890 and tetraethylorthosilicate ($Si(OC_2H_5)_4$) TEOS were purchased From Aldrich-Sigma. Detailed nomenclature including chemical formulas of the whole surfactants used is given in Table 1. Deionized water and hydrochloric acid (1N-HCl) have been used for each synthesis; the 1N-HCl was prepared from 37% fuming hydrochloric acid (Aldrich-Sigma).

Table 1: Physicochemical properties of surfactants nonyl-phenyl-ethers type commercialized under the designation IGEPAL® CO-890, Brij®35, Brij®78 an Brij®98

Commercial name	Chemical formula	Molar weight / $g.mol^{-1}$	HLB (*)
IGEPAL® CO-890	$C_9H_{19}-C_6H_4-(OC_2H_4)_{40}-OH$	1982	17
Brij®35	$C_{12}H_{25}-(OC_2H_4)_{23}-OH$	1199.6	16.9
Brij®78	$C_{18}H_{37}-(OC_2H_4)_{20}-OH$	1151.5	15.3
Brij®98	$C_{18}H_{35}-(OC_2H_4)_{20}-OH$	1149.5	15.0

(*) hydrophilic-lyophilic balance

Synthesis of sorbents

The synthesis protocol adopted in this work consists of mixing an aqueous solution of the surfactant with a 1N-HCl solution with constant stirring for 60 minutes. The TEOS was added to this mixture and left under stirring for 24 hours at room temperature. The mixture was then heated at $100^\circ C$ overnight without stirring. The precipitated solid product was recovered by filtration, washed and dried at $80^\circ C$. For example, 2 g of Brij®98 in 30 g of demineralized water was stirred for 10 minutes before adding 120 ml of 1N-HCl solution. 9 g of TEOS was added to this homogeneous mixture and kept under vigorous stirring for 24 hours. The mixture was then introduced into a sealed tube and heated at $100^\circ C$ for 48 or 72 hours. The resulting precipitated solid product was recovered by filtration, washed and dried. Calcination of the obtained



fine white powder was carried out in a tube furnace at 550°C in air; this temperature was reached with a heating rate of 10°C/min and a first plateau at 100°C for 1h. After the second plateau at 550°C for 6h, the oven was cooled down at room temperature with a cooling rate of about 5°C/min. In all reaction mixtures, we have kept the same amount of TEOS, H₂O and HCl while we have used two different weights (2 and 4 g) for the surfactants and the duration of the hydrothermal treatment was stated at 48 or 72 hours (Table1).

Characterization

Structural characterization was performed using a Rigaku Ultima IV high resolution X-ray powder diffractometer (XRD) using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). The X'PERTPLUS[®] software enabled the counting of the spectra and the calculation of pore-pore distance by indexing the reflections. The characterization of pores was essentially obtained from nitrogen (N₂) sorption-desorption isotherms recorded at 77 K by using a fully automated apparatus ASAP 2020 (Micromeritics). Before each measurement, the sample was outgassed under vacuum (<3 $\mu\text{m Hg}$) at 400°C overnight. Specific surface areas were calculated by applying the BET model in the P/P₀ range of 0.1-0.3. The data were analyzed by BJH (Barrett, Joyner and Halenda) method using the Halsey equation for multilayer adsorption. The pore size distribution was obtained from the desorption branch of the isotherm and the pore volume was calculated at the elevated relative pressure P/P₀ =0.99. Morphology and particle size of the final products were observed by using scanning electron microscopy FE-SEM (JEOL JSM-6340F) and transmission electron microscope TEM (JEOL JEM-2010).

Adsorption of CO₂

Adsorption isotherms of CO₂ were measured on the same ASAP 2020 (Micromeritics) apparatus at 0 °C. Sample cell was loaded with ca. 300 mg of the sorbent. Before the sorbent was outgassed in vacuum at 400 °C for 4 h in order to remove any adsorbed impurities, the adsorption run was carried out using highly pure CO₂ (99.999%) in a pressure range from 5-760 mm Hg. Maximum amount of adsorbed CO₂ (Q_m) was determined by Langmuir equation using molecular cross-sectional area (0.17 nm²) for CO₂. Both Langmuir and Freundlich models were applied for elucidating the physical significances of the conducted model and the extracted parameters.

We propose also, a general kinetic model to describe the adsorption of CO₂ on pure siliceous samples at 0 °C. The equation of adsorption rate at the pseudo order n¹⁷ that was used can be expressed in its general form:

$$\frac{\delta q_t}{(q_e - q_t)^n} = k \cdot dt$$

Where q_e and q_t are the sorption capacity at equilibrium and at time, respectively, and k is the constant rate. This equation stems from the modified Avrami's kinetic equation which implies several steps¹⁷. Its linear form is deduced by integrating the equation rate

$$(q_e - q_t)^{1-n} = q_e^{1-n} + k(n - 1)t.$$

The least squares criterion was used to determine the model parameters. To check the adequacy of the model, the coefficient of correlation R² between the experimental and calculated data was determined. We have also checked that the value of q_e calculated by the theoretical model fit to the experimental value obtained from the Langmuir model applied to adsorption measurements of CO₂ at 0 °C.

RESULTS AND DISCUSSION

For all samples except Has-6, XRD patterns recorded on calcined samples show the presence of a broad peak in the 2 θ range of 1-4°, which indicates a poorly ordered mesostructure such as observed for mesostructured solids with worm-like pores (Pauly and Pinnavaia, 2001) (Figure 1). The XRD pattern of Has-6 sample shows a first peak narrower and a second very broad peak, indicating a more ordered pore network. These two XRD peaks can be indexed in (100) and (200) reflections indicating a poorly ordered 2D hexagonal mesostructure. If the correlation distance deduced from the main XRD peak (the first one for Has-6 sample) can be attributed to the pore-pore distance, an expansion of the silica matrix was observed when synthesis duration was increased from 48 to 72H. The expansion of the silica matrix is of about 9% for syntheses realized with IGEPAL®CO-890 (Has-1 and Has-2), and of about 40% for those realized with Brij®35 (Has-4 and Has-5) (Table 2).

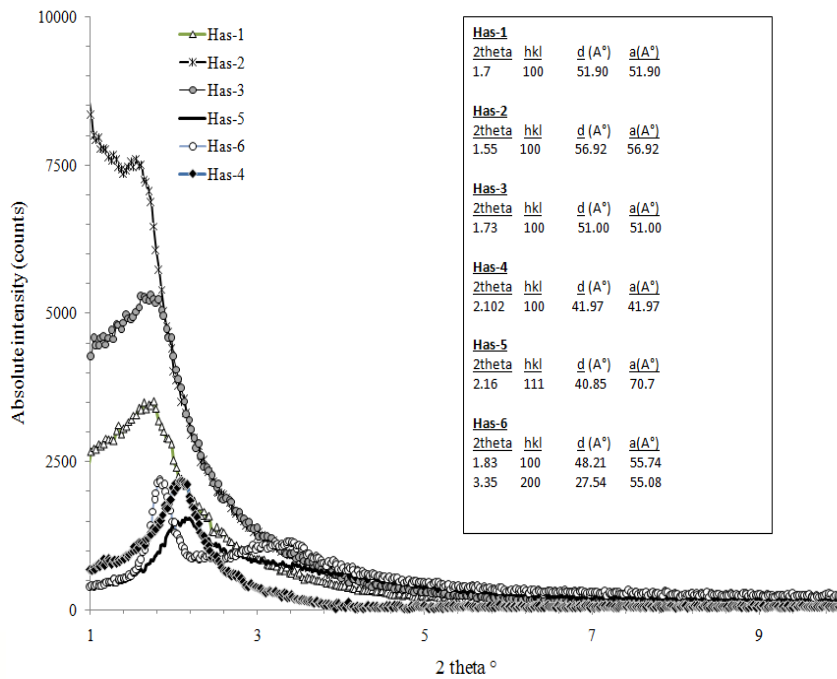


Figure 1: Low-angle XRD patterns of calcined samples: Has-1(2g CO-890; 48h), Has-2(2g CO-890; 72h), Has-3 (4g CO-890; 48h), Has-4 (2g Brij35;48h) , Has-5 (2g brij35;72h), Has-6 (2g brij98;48h) and Has-7 (2g brij78;48h).

Table 2: Textural and structural parameters of materials calcined at 550°C under air for 6 hours. * used with 30g H₂O; 120 ml HCl; 9g TEOS; ^ad value of characteristic reflection of the calcined products. ^b Calculated at P/P°=0.99; ^c Pore diameter calculated from desorption branch with BJH method. ^d Calculated from $t = (D_{pore-pore} - \emptyset)$; ^e () microporous specific surface.

Designation	Surfactant mass (duration at 100 °C)	D _{pore-pore} / A° ^a	S _{BET} /m ² .g ⁻¹	V _P /cm ³ .g ⁻¹ ^b	∅ / A° ^c	Thickness ^d /A°
Has-1	2 g CO-890 (48h)	51.9	659 (0) ^e	0.58	43.0	8.9
Has-2	2 g CO-890 (72h)	56.9	664 (0) ^e	0.65	43.0	13.9
Has-3	4 g CO-890 (48h)	51.0	757 (0) ^e	0.37	43.2	6.8
Has-4	2 g Brij35 (48h)	42.0	1221 (52)	0.45	28.2	13.8
Has-5	4 g Brij35 (72h)	70.7	800 (42) ^e	0.78	58.0	12.7
Has-6	2 g Brij98 (48h)	55.5	675 (33) ^e	0.48	37.5	18.0
Has-7	2 g Brij78 (48h)	55.7	760 (38) ^e	0.54	44.0	11.7

SEM observations done on samples Has-4 and Has-2 (Figure 2) that were synthesized from brij35 and IGEPAL®CO-890, respectively, for the same molar composition, show distinct spherical particles for Has-4 with mean diameter of 2-4µm and entangled small particles (< 1µm) with pseudo cubic shape for Has-2. Worm-like mesoporous texture was clearly observed by TEM for both samples that are usually observed with such surfactants (Su Kim et al., 2000).

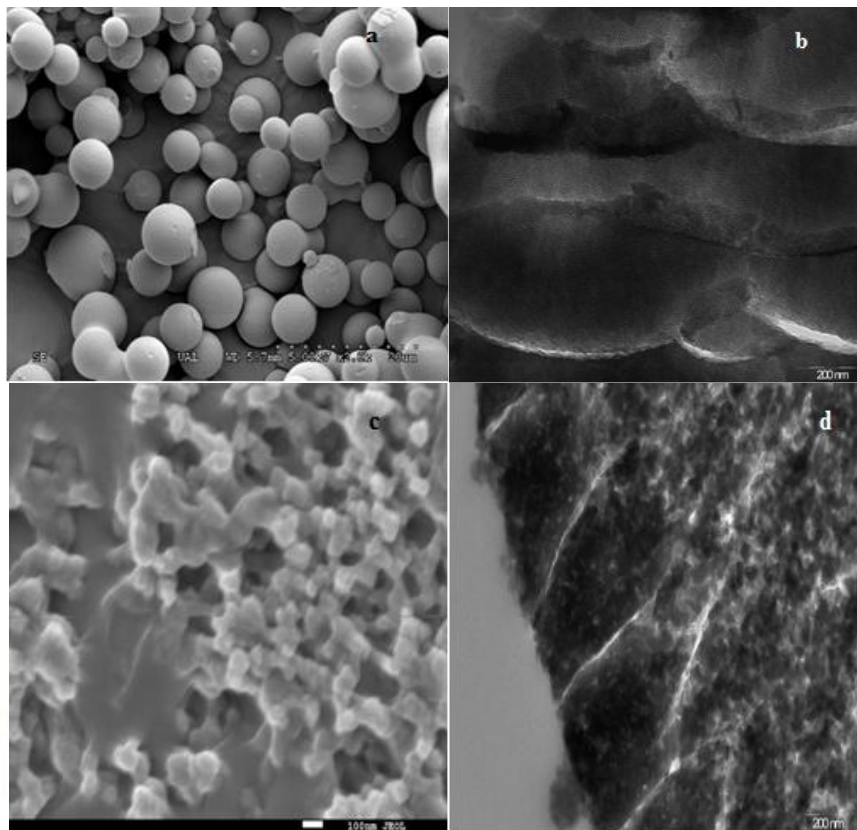


Figure 2: Scanning electron micrographs (SEM) of (a) Has-4 and (c) Has-2 and Transmission electron micrographs (TEM) of (b) Has-4 and (d) Has-2.

Nitrogen adsorption/desorption isotherms are type IV for all samples. N_2 adsorption/desorption isotherms of samples Has-4 et Has-5, both synthesized with the same molar composition at 100°C for 48 and 72h, respectively, are reported in figure 3. The N_2 adsorption/desorption isotherm of Has-4 has no hysteresis indicating open uniform cylindrical mesopores ($\sim 28 \text{ \AA}$). Higher quantities of adsorbed N_2 were observed for Has-5 with a hysteresis of type H2 suggesting narrow diameters at the extremities of pores. Textural parameters are reported in Table 2. Materials made from IGEPAL[®]CO-890 have the same mean diameter of 43 \AA without any micropores. It seems that the surfactant molecule which has a hydrophilic chain constituted of 40 ethylene oxide segments is subject of torsions resulting in size reduction before forming micelles. On the other hand, materials made from Brij[®]35, Brij[®]78 and Brij[®]98, present micropores that probably interconnect mesopores with diameters of about $30\text{-}60 \text{ \AA}$ depending on the synthesis parameters.

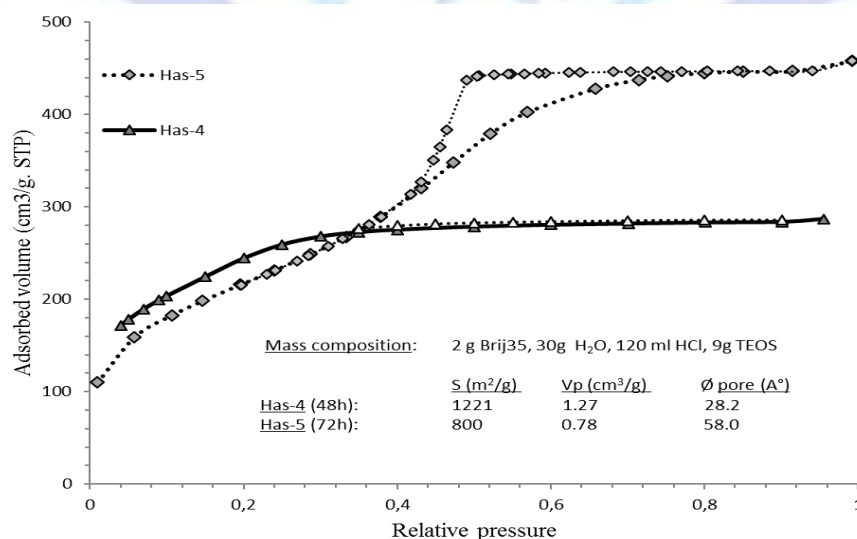


Figure 3: Nitrogen adsorption/desorption isotherms at 77 K of calcined samples. Insert: pore size distribution (PSD) obtained by BJH method applied on desorption branch.



The adsorption of CO₂ à 0 °C measured on siliceous solids shows a regular variation of adsorbed amounts until upper limit of pressure (760 mm Hg) with an optimal adsorption capacity (8.50 mmol/g) for material Has-4 (Figure 4). This latter has a much larger specific surface area (~1220 m²/g) than other solids (Table 2).

Tableau 3: Langmuir and Freundlich constants for mesoporous silica samples.

Designation	Langmuir			Freundlich		
		k (10 ⁻⁴)	R ²	K _F	1/n	R ²
Has-1	40.3	16.2	0.978	0.134	0.803	0.999
Has-2	94.1	13.3	0.962	0.266	0.812	0.996
Has-3	190.0	8.00	0.918	0.260	0.871	0.998
Has-4	371	9.07	0.979	0.787	0.843	0.997
Has-5	61.4	9.34	0.979	0.089	0.880	0.998
Has-6	39.5	13.8	0.974	0.103	0.825	0.997
Has-7	42.3	16.07	0.976	0.138	0.804	0.996

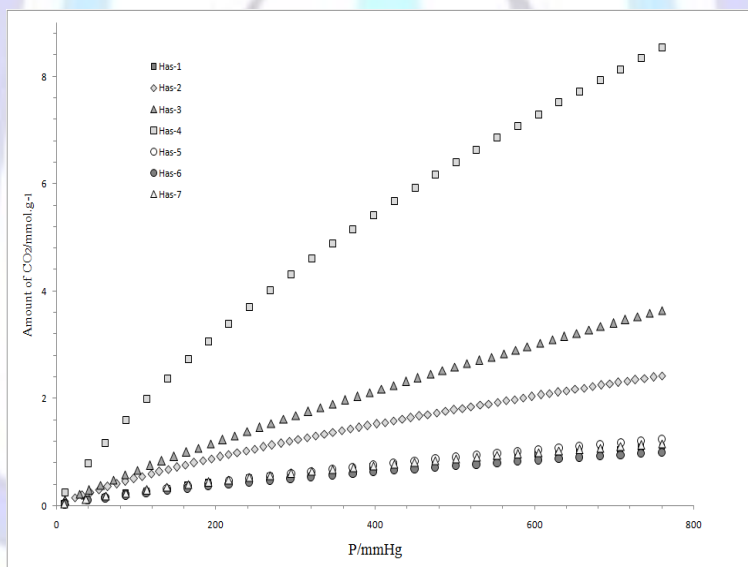


Figure 4: Carbon dioxide adsorption isotherms at 0 °C.

The Freundlich model seems to be more appropriate to describe the CO₂ adsorption than the Langmuir model, indeed in this first case the R² values are closed to 1 as shown in Figures 5 and 6. Furthermore, the parameters obtained from the two models are given in Table3, where the constant K_F reflects better the adsorption.

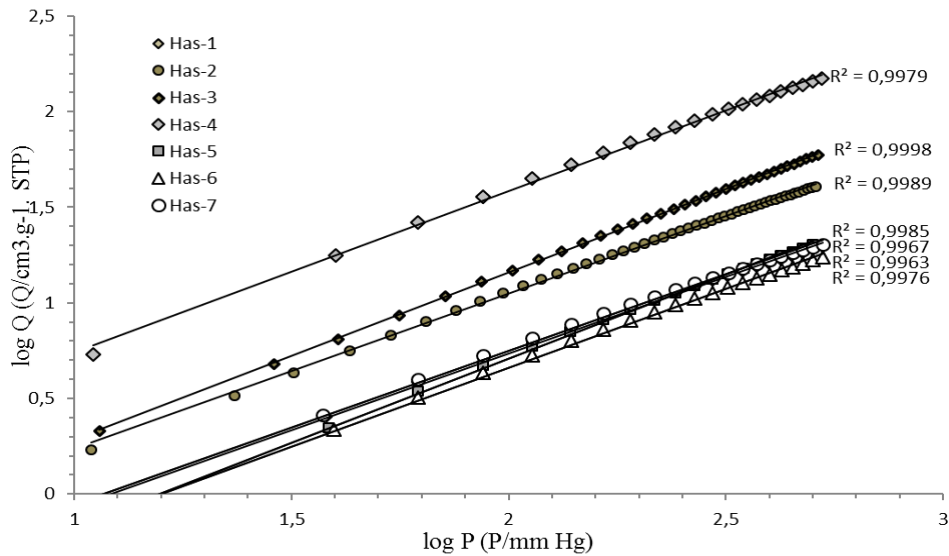


Figure 5: Freundlich model of CO₂ adsorption isotherms.

The value of the parameter n ($1.25 > n > 1.14$) in the Freundlich equation suggests that the adsorption occurs as monolayer on the external surface of the solid but it allows the filling of the mesopores by a multilayer adsorption in agreement with their large size. The difference in the adsorbed amounts of CO₂ for each material can be explained by the nature of the pores; high in Has-4 where mesopores are large and uniform, so fully open at the extremities, but low in Has-5 where mesopores are not regular with narrowing that reduce the adsorption of CO₂ inside pores.

Table 4 summarizes the kinetic model parameters of CO₂ adsorption at 0°C, educed from curves reported in figure 6 and reflects a pseudo-order of the adsorption rate.

Tableau 4: Values of the kinetic model parameters of CO₂ adsorption at 0 °C.

Designation	n	K	$Q_{e_{exp}}$	$Q_{e_{pred}}$	%	R ²
Has1	1.90	$1.11 \cdot 10^{-3}$	40.3	41.3	0.02	0.981
Has2	3.22	$4.50 \cdot 10^{-7}$	94.1	95.3	1.32	0.997
Has3	2.98	$4.55 \cdot 10^{-7}$	190.0	194.3	2.31	0.982
Has4	2.55	$3.22 \cdot 10^{-6}$	371.1	374.9	1.04	0.989
Has5	2.51	$3.31 \cdot 10^{-5}$	61.4	61.2	0.31	0.985
Has6	2.00	$1.02 \cdot 10^{-4}$	39.5	41.7	5.45	0.989
Has7	1.94	$1.07 \cdot 10^{-3}$	42.3	42.6	0.71	0.980

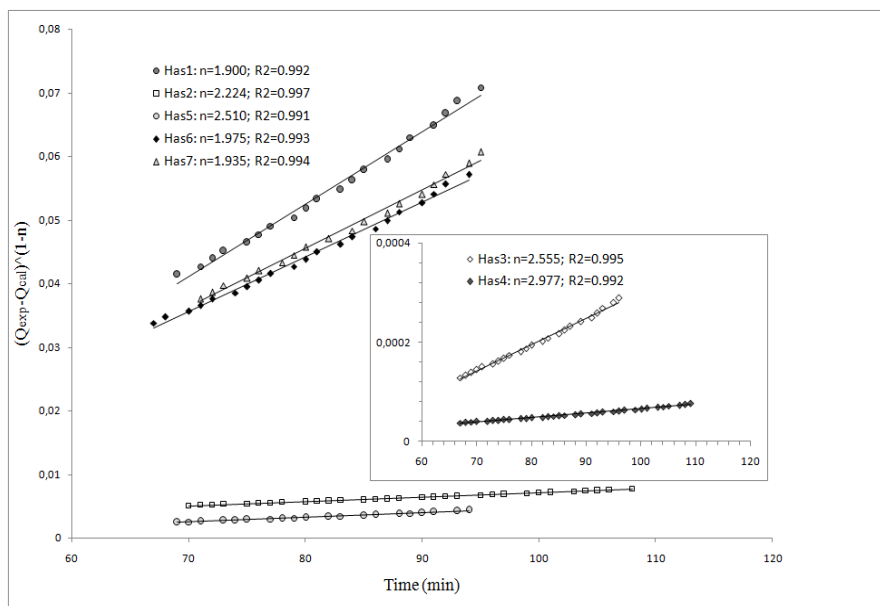


Figure 6: Pseudo-order n kinetic model for CO_2 adsorption at 0°C .

The use of the theoretical equation based on the modified Avrami's model lead to values of n from 1.90 to 2.97; those are obtained for a minimal value of $(Q_{e_{exp}} - Q_{e_{pred}})$ with R^2 superior to 0.98, thus with a good correlation between experimental data and the theoretical model. It is shown that the CO_2 adsorption rate is fast, even if the desorption phenomenon at the level of the external pure siliceous surface reduces the adsorption capacity.

CONCLUSION

Spherical silica particles with radial mesopores were synthesized by using non-ionic surfactants as template and tetraethylorthosilicate (TEOS) as silica precursor. Textural characterization shows a high specific surface for samples, especially for those obtained with a low molar ratio Brij@35/TEOS ($\sim 1220 \text{ m}^2/\text{g}$), which are characterized by a microporosity unlike other samples are only mesoporous. Samples exhibit a better CO_2 adsorption at 0°C and the Freundlich adsorption model was found to have the highest regression value and to hence the best fit. This study presents a kinetic analysis of CO_2 adsorption and the proposed model was in good agreement with experimental data.

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