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CO_2 sorption onto silica mesoporous materials made from nonionic surfactants

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ABSTRACT

Spherical mesoporous silica particles were successfully prepared by using non-ionic amphiphilic di-block co-polymers C_nH_{2n+1}-$(EO)_x$-OH as templates and tetraethylorthosilicate (TEOS) as silica precursor. The synthesized mesoporous silica materials were characterized by X-ray diffraction (XRD), N_2 adsorption–desorption and scanning electron microscopy (SEM) techniques. CO_2 adsorption at 273 K was evaluated by a volumetric method, and the CO_2 sorption behavior was described by applying both Langmuir and Freundlich equations. Results indicate a high adsorption capacity of CO_2 (5–9 mmol/g), depending essentially on the porous texture of the materials. An adsorption kinetic model was used to describe the adsorption of CO_2 over template-free mesoporous siliceous materials. A good agreement with experimental data was found.

1. Introduction

Discovered in the early 90's [1,2], 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 $(EO)_x(PO)_y(EO)_x$ (with EO = $-CH_2CH_2O-$; PO = $-CH_2CH(CH_3)O-$) [3–5] and di-block copolymers $C_nH_{2n+1}-(EO)_x$ [6–9], 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. [10] 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 $C_nH_{2n+1}(EO)_x$ 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 $C_{16}H_{33}(EO)_x$ leads to lamellar ($x = 6$), 2D slightly distorted hexagonal, disordered ($x = 10$), and cubic ($x = 20$) mesostructures.

Sequestration of CO_2 in fossil-fuel power plants stack gas and other industrial gases is required to mitigate the impact of greenhouse gas on the world climate. Separation of carbon dioxide (CO_2) from gaseous mixture is also an important issue for the removal of CO_2 in natural gas processing and power plants. The 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 [11]. In recent years, research activities have been focused on the study of CO_2 adsorption on zeolites [12], activated carbon [13], metal-organic frameworks [14], amine-

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modified materials [15–17] and membranes [18]. More recently, Hao et al. [19] 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 the synthesized materials as sorbents.

In the present work, a set of spherical 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 273 K.

2. Experimental

2.1. Chemicals

Polyoxyethylene (20) oleyl ether ($C_{18}EO_{20}$) named Brij®98, polyoxyethylene (20) stearyl ether ($C_{18}EO_{20}$) named Brij®78 and polyoxyethylene (23) lauryl ether ($C_{12}EO_{23}$) named Brij®35 surfactants have been provided by ACROS Organics Inc. Polyoxyethylene (40) nonylphenyl ether, branched ($C_{15}EO_{40}$) named IGEPAL®CO-890 and tetraethylorthosilicate ($Si(OC_2H_5)_4$) named 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 HCL 1 mol L^{-1} have been used for each synthesis; the aqueous HCL 1 mol L^{-1} solution was prepared from 37% fuming hydrochloric acid (Aldrich–Sigma).

2.2. Synthesis of sorbents

The synthesis protocol adopted in this work consists of mixing an aqueous solution of the surfactant with an aqueous HCL 1 mol L^{-1} solution at constant stirring for 60 min. The TEOS was added to this mixture that was left under stirring for 24 h at room temperature. The mixture was then heated at 100 °C overnight without stirring. The precipitated solid product was recovered by filtration, washed and dried at 80 °C. For example, 2 g of Brij®98 in 30 g of demineralized water was stirred for 10 min before adding 120 ml of HCl 1 mol L^{-1} solution. 9 g of TEOS was added to this homogeneous mixture that was kept under vigorous stirring for 24 h. The mixture was then introduced into a sealed tube and heated at 373 K for 48 or 72 h. 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 823 K in air; this temperature was reached with a heating rate of 10 °C/min and a first plateau at 373 K for 1 h. After the second plateau at 823 K for 6 h, the oven was cooled down at room temperature with a cooling rate of about 5 K/min. In all reaction mixtures, we have kept the same amount of TEOS, H_2O and HCl while we have used two different weights (2 and 4 g) of surfactants and the duration of the hydrothermic treatment was stated at 48 or 72 h (Table 2).

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

Commercial name	Chemical formula	Molar weight/g mol^{-1}	HLB[a]
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

[a] Hydrophilic-lyophilic balance.

Table 2
Textural and structural parameters of materials calcined at 823 K under air for 6 h.

Designation	Surfactant mass[f]	$D_{pore-pore}$[a]/ Å	S_{BET}/ $m^2\ g^{-1}$	V_p[b]/ $cm^3\ g^{-1}$	Ø[c]/ Å	t[d]/Å
Has-1	2 g CO-890 (48 h)	51.9	659 (0)[e]	0.58	43.0	8.9
Has-2	2 g CO-890 (72 h)	56.9	664 (0)[e]	0.65	43.0	13.9
Has-3	4 g CO-890 (48 h)	51.0	757 (0)[e]	0.37	43.2	6.8
Has-4	2 g Brij35 (48 h)	42.0	1221	0.45	28.2	13.8
Has-5	4 g Brij35 (72 h)	70.7	800 (42)[e]	0.78	58.0	12.7
Has-6	2 g Brij98 (48 h)	55.5	675 (33)[e]	0.48	37.5	18.0
Has-7	2 g Brij78 (48 h)	55.7	760 (38)[e]	0.54	44.0	11.7

[a] Corresponding to the *d* value of the characteristic X-ray reflection of the calcined products.
[b] Calculated at $P/P^\circ = 0.99$.
[c] Pore diameter calculated from desorption branch with BJH method.
[d] Wall thickness $= D_{pore\text{-}pore} - Ø$.
[e] ( ) Microporous surface.
[f] Used with 30 g of H_2O: 120 ml HCl: 9 g TEOS.

2.3. Characterization

Structural characterization was performed using a Rigaku Ultima IV high resolution X-ray powder diffractometer (XRD) using CuKα radiation ($\lambda = 1.5418$ Å). The X'PERTPLUS© software enabled the counting of the diffractograms and the calculation of pore–pore distance by indexing the reflections. The characterization of pores was essentially obtained from nitrogen (N_2) 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 μm Hg) at 623 K overnight. Specific surface areas were calculated by applying the BET (Brunauer, Emmett and Teller) model in the P/P_0 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 $P/P_o = 0.99$. Morphology and particle size of the final products were observed by using field-emission scanning electron microscopy FE-SEM (JEOL JSM-6340F) and transmission electron microscope TEM (JEOL JEM-2010).

2.4. Adsorption of CO_2

Adsorption isotherms of CO_2 were measured on the same ASAP 2020 (Micromeritics) apparatus at 273 K. Sample cell was loaded with ca. 300 mg of the sorbent. Before experiments the sorbent was outgassed in vacuum at 623 K for 4 h in order to remove any adsorbed impurities. The adsorption run was carried out using highly pure CO_2 (99.999%) in a pressure range from 5 to 760 mm Hg. Maximum amount of adsorbed CO_2 (Q_m) was determined by Langmuir equation using molecular cross-sectional area (0.17 nm^2) for CO_2. Both Langmuir and Freundlich models were applied for elucidating the physical significances of the conducted model and the extracted parameters. CO_2 adsorption isotherms for all adsorbents are examined by fitting the experimental data to Langmuir (Eq. (1)) and Freundlich (Eq. (2)) isotherm models:

$$q_e = \frac{q_m k_A P}{(1 + k_A P)} \tag{1}$$

$$q_e = K_F P^{1/n_F} \tag{2}$$

where P (mm Hg) and q_e (cm^3 STP/g) are the gas phase pressure and solid phase adsorption quantity of carbon dioxide at equilibrium, respectively; k_A is the Langmuir isotherm constant (1/mm Hg); q_m