



Silver nanoparticle-containing submicron-in-size mesoporous silica-based systems for iodine entrapment and immobilization from gas phase



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ABSTRACT

Submicron-in-size silica particles with controllable morphology, particle size and mesoporosity, have been prepared under basic conditions making use of cationic alkyltrimethylammonium surfactants (C_n TAB, $n = 12, 16, 18$) as porogens. Gaseous nitrogen adsorption, XRD and TEM experiments revealed quasi-spherical homodispersed objects possessing regular mesopores of the MCM-41 type; lengthening of the hydrophobic tail of the template resulted in smaller particles with greater intraparticle pores. The aggregation and sintering of individual silica particles during the calcination step led to the formation of particle clusters comprising interparticle voids, as evidenced by the ¹²⁹Xe NMR and TEM studies. The calcined particles were subsequently loaded with metallic silver. The measurements of iodine adsorption onto Ag-functionalized materials from the gas phase were supplemented by XRD, SEM/EDX, and TGA/DTA studies. It was demonstrated that the functionalized silica retained much gaseous iodine in an irreversible manner, mainly as an 'interfacial' AgI. The best compromise between the textural parameters and the post-synthesis functionalization was obtained for the large-pore silica templated with C_{18} TAB. Indications about the presence of silver metal nanoparticles, displaying certain heterogeneity in size and shape, within the pores of this sample were given based on the analysis of ¹²⁹Xe NMR spectra supplemented by UV-Visible absorption spectra and powder XRD patterns in the wide-angle region. The material can be recommended for the entrapment and immobilization of radioactive iodine in the nuclear industry since it guarantees that the adsorbed pollutant is primarily localized within the material pores and is thermally stable up to 800 K in air.

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1. Introduction

One of the most serious and persistent problems of safe nuclear power is related to the capture of radiological fission gasses formed during nuclear fuel reprocessing or nuclear fallout [1,2] since such gasses may potentially become a fugitive emission. Among the various constituents of the off-gas, radioactive iodine is a significant contributor to the health hazards because of its high mobility in the environment, its easy assimilation by living organisms, and its involvement in human metabolic processes. Besides a reduction in radioactivity release into the environment and generated waste volume, the fundamental goal in developing processes for gas

phase capture of iodine is also to provide simple systems with high capture efficiency, lower maintenance costs and sufficient stability for long-term storage.

Two types of capture technology have been studied over the years: absorption of gaseous constituents by scrubbing into a liquid solvent and gas adsorption on an appropriate solid matrix [3]. The scrubbing technology, e.g., with an alkaline solution, generates a liquid residue which usually is to be transformed into a stable waste form suitable for disposal or eventual sequestration. This essentially means that the dissolved radioiodine should be converted to a form insoluble in ground water, e.g., Pb, Ag, and Hg iodides or hydrotalcite-like Bi-I-oxide compounds formed by iodide or iodate encapsulation in layered metal oxide-hydroxide anion scavengers [4–6]. The solid materials tested for the removal of gaseous iodine compounds by adsorption from the gas phase

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include macroreticular resins, silver-loaded zeolites, silica or alumina, and metal–organic frameworks (MOFs) [7–13]. The sorption technology offers some advantages over liquid scrubbing as being generally more simplistic in design and implementation, more efficient with respect to very low iodine concentrations in the off-gas, and giving the possibility of sorbent regeneration.

Compared to organic materials (e.g. macroreticular resins), silica-based substrates are generally more stable to radiolysis and they can operate safely at elevated temperatures [14]. Despite the high cost of silver, silver iodide has a low solubility in water and in aqueous solutions [15,16] on which to base the long-term storage technology. Nevertheless, the relatively high vapour pressure of liquid AgI above the melting point at 825 K [16] and its potential mobility limit the maximum processing temperature. Therefore, the immobilization of AgI within the pores of a solid adsorbent after the iodine entrapment by silver-loaded materials may improve the overall stability of the ultimate waste form [12]. The use of mesopores materials as matrix hosts is more appropriate than that of microporous zeolites where the iodine diffusion was found to be slow, thereby limiting the adsorption phenomenon [14,17].

The present paper attempts to explore the capacity of silver-derivatized silica particles, with controllable morphology, particle size, mesoporosity, and incorporation of the active phase at the internal surface, for capturing elemental iodine from the gas phase. The surfactant-templating synthesis approach described previously [18,19] was adapted here to synthesize porous submicron-in-size silica spheres under basic conditions. Calcined mesoporous silica particles were subsequently functionalized by impregnation with silver nitrate as a silvering agent with a view of developing pre-shaped adsorbents which contained Ag nanoparticles within the mesopores. Three quaternary ammonium surfactants were tested as structure directing agents. Their impact on the particle porosity and morphology, accessibility of the resulting porous structure and distribution of the silver active phase were determined. The comparison of the capacity and reversibility of gaseous iodine adsorption between the functionalized and non-functionalized samples allowed the benefic impact of the silver nanoparticles on the materials performance to be demonstrated. The ultimate selection of the best silver-silica particles system for the specific application in the area of nuclear industry was guided by the feasibility of irreversible and temperature-stable capture of gaseous iodine in large quantities inside the porous structure of mineral particles.

2. Experimental

2.1. Chemicals

The following chemicals, tetraethyl orthosilicate (TEOS, 99%), dodecyltrimethylammonium bromide (C_{12} TAB, 95%), hexadecyltrimethylammonium bromide (C_{16} TAB, 95%), octadecyltrimethylammonium bromide (C_{18} TAB, 97%), sodium hydroxide (NaOH, 98%), and silver nitrate ($AgNO_3$, 99%), iodine (I_2 , 99.99%) were purchased from Sigma–Aldrich and used without further purification.

2.2. Materials preparation

Mesostructured silica objects were synthesized under basic conditions [18] making use of cationic alkyltrimethylammonium surfactants as structure directing agents and TEOS as a silica source. In a typical synthesis, 0.2 g of C_{12} TAB (or 0.05 g of C_{16} TAB or C_{18} TAB) was dissolved in 50 g of deionized water under constant stirring at room temperature. 575 μ L of TEOS were poured into the solution and the temperature was raised up to 313 K. Then 350 μ L of NaOH (2 M) were added to the resulting clear solution and the mixture was subsequently stirred for 2 h. The resulting solid was

collected by centrifugation and washed with distilled water and ethanol. The removal of the surfactant template was performed by calcination in air at 823 K during 6 h with a heating rate of 1 deg min^{-1} . The calcined samples were subsequently used for *in situ* synthesis of silver nanoparticles within the mesopores. For this purpose, 45 mg of a given sample were dispersed in 10 mL of a 3.6 mmol L^{-1} $AgNO_3$ solution in a 1:3 mixture of ethanol and water, and stirred during 12 h at 313 K. The resulting solid phase was removed by centrifugation and a silver reduction was carried out in 10 mL of a 0.1 mmol L^{-1} aqueous $NaBH_4$ solution during 30 min at room temperature. The final gray solid was dried under vacuum during 10 h at 373 K.

2.3. Materials characterization

Scanning electron micrographs (SEM) and transmission electron micrographs (TEM) were obtained with a Hitachi S-2600N (using a secondary electron scintillator as detector) and a JEOL 1200 EX microscope, respectively. For the purpose of TEM analysis, the sample particles were dispersed in ethanol and then dropped onto copper grids with porous carbon films. The specific surface area and pore structure parameters of the materials studied in the present work were determined from the measurements of nitrogen adsorption–desorption at 77 K with the use of a Micromeritics Autochem ASAP 2020 V3.00 H unit. Prior to the sorption experiment, the sample (about 40 mg) was evacuated under vacuum at 523 K for 12 h. Small-angle powder X-ray diffraction (XRD) measurements were performed with a PANalytical X'Pert MPD (Philips 1710) diffractometer controlled by a computer. The XRD patterns were collected using a $Cu K\alpha$ radiation, the 2θ diffraction angles being recorded at a rate of 0.5 deg min^{-1} in the range from 1° to 7° . For some selected samples containing silver, the XRD experiment was continued in the 2θ range up to 80° . In the latter case, the acquisition time was varied from 4 to 14 h in order to increase the signal-to-noise ratio and obtain clearly visible peaks in the XRD patterns. ^{129}Xe -NMR spectra were obtained at 297 K using an AC 250L Bruker spectrometer operating at a Larmor frequency of 69.19 MHz (15,000 signal acquisitions, recycle delay of 8 s between $\pi/2$ pulses). The powder of a given sample was loaded in a special NMR tube (10 mm o.d.) fitted with a re-sealable valve suitable for attachment to a vacuum line. The resulting sample (the maximum height of the powder column inside the NMR tube was 20 mm) was first evacuated for 1 h at room temperature, and then heated during 10 h at 573 K under vacuum corresponding to 10^{-3} Pa. It was subsequently equilibrated with gaseous xenon at a constant pressure ranging between 0.5 and 133 kPa at room temperature. The chemical shifts measured with a precision of 0.5 ppm were referenced with respect to the ^{129}Xe gas resonance ($\delta = 0$ ppm) corrected to the xenon density limit. Sample spinning and field locking were not used. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out on a SETARAM Labsys apparatus in order to study changes in the chemical properties of the pristine samples and those containing Ag species as a function of increasing temperature. A given mass of solid sample was placed in a 80 μ L alumina crucible. The TGA and DTA curves were obtained up to 873 K in flowing nitrogen using a constant heating rate of 10 deg min^{-1} . Ultraviolet–visible (UV–Vis) absorption spectra were collected with the aid of an UV–visible Jasco V-670 spectrophotometer.

2.4. Gaseous iodine adsorption and desorption

Iodine adsorption experiment was performed in a saturation mode using gaseous iodine obtained by the sublimation of iodine crystals placed inside a thermostated dryer at 308 K (the iodine vapor pressure is about 133 Pa at 312 K according to the

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