Preparation of nanostructured TiO_2 in supercritical CO_2 media – Estimation of their sorption properties

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ABSTRACT

A batch method has been recently developed by the authors for the preparation of mesoporous micrometric TiO_2 powder. This technique is based on the thermal decomposition of titanium isopropoxide in a mixture of SC CO_2 and isopropanol at 30 MPa, in acidic conditions. The textural properties of powders can be controlled by varying the synthesis temperature in the range 150-350°C. The formed TiO_2 particles are spherical and consist of aggregated crystallites whose size is between 5 and 17 nm. Powders are mesoporous, with high specific surface areas in the range 90-280 m^2/g. Strontium extraction tests revealed that the TiO_2 powders prepared in SC CO_2 media have better sorption capacity than the commercial Degussa powder P25 and are effective for the sorption of radionuclides in liquid wastes.

INTRODUCTION

Nuclear facilities generate significant amounts of radioactive liquid effluents. Contaminated aqueous effluents might contain various radionuclides with high radioactivity. It is necessary to extract these radioactive ions to ensure the protection of human health and environment. Inorganic sorbents, such as zeolites or ceramic oxides, are commonly used in the treatment of aqueous nuclear wastes because of their high selectivity, their thermal and chemical stability and their irradiation resistance [1]. Due to its attractive surface properties with isoelectric point around 6 and low solubility over a wide pH range (2-12) [2], titanium dioxide (TiO_2) is an effective inorganic sorbent for negatively and positively charged radioelements. Their sorption properties depend on various parameters like textural properties and experimental conditions (pH, salts nature and concentration) [3, 4]. A decrease in TiO_2 crystallite size improves their specific surface areas, thereby increasing the number of adsorption sites and the involved surface energies at the nanometric scale. Thus, the sorption capacities of nanomaterials are usually improved in comparison with conventional materials [5]. Mesoporous powders, with high surface to volume ratio, are also beneficial for decontamination application because of the improved access to the active sites. Synthesis of nanostructured TiO_2, with high surface area and a well-defined mesoporous network, is consequently one of the key points which deserve attention in the development of decontamination processes by sorption. In the last decades, supercritical (SC) CO_2 has proven several advantages for the synthesis and processing of various inorganic nanostructured materials [6, 7]. The preparation of TiO_2 sorbent materials in SC CO_2, resulting in high specific surface areas, seems promising to improve waste treatment process

MATERIALS AND METHODS

Chemicals

Titanium (IV) isopropoxide (TIP) (Sigma-Aldrich, 97 % purity) was used as ceramic precursor without further purification. Additional reactants were used: nitric acid (HNO_3) (Sigma-Aldrich, 69 %) as sol stabilizer and isopropanol (Sigma-Aldrich, 99.9 % purity) as co-solvent. The CO_2 was used as received from Air Liquide (99.998 % purity, water amount = 3 ppmv). Both deionized water and strontium nitrate $Sr(NO_3)_2$ (Sigma-Aldrich, 99% purity) were used for sorption experiment and 0,5 M KOH solution to adjust the pH.

Batch reactor and powder preparation

TiO_2 powders were synthesized in SC CO_2 media using a batch mode reactor (Figure 1). TiO_2 powders were obtained by thermal decomposition of a TIP solution in SC CO_2. The TIP solution was prepared by mixing 50 mL of isopropanol and 10 mL of TIP and adding 5 mL of nitric acid. The sol was stirred for 1 min under atmospheric conditions and poured in the reactor. The reactor was rapidly closed and CO_2 was injected to reach a pressure of about 6 MPa. The temperature regulating device was turned on. The pressure increased with the temperature. The selected conditions of pressure and temperature were then set and maintained for 1 hour. While the pressure was always maintained at 30 MPa for all experiments, the reaction temperature was set either at 150°C (sample #DT150), 250°C (#DT250) or 350°C (#DT350) in order to investigate the influence of this parameter on the powder textural and structural properties. Finally, the reactor was depressurized and the temperature was decreased back to room temperature. The recovered (as-synthesized) powders were dry and ready to be characterized.

Characterizations

TiO_2 powder crystalline structure was investigated by X-ray diffraction (XRD, X'PertPRO-LANalytical) using Cu Kα radiation. Crystallite sizes and shapes were observed using a transmission electron microscopy (TEM, JEOL 200CX). Sample morphology was characterized by field emission scanning electron microscopy (FE-SEM Hitachi S4800). Particle size distributions were evaluated from micrograph analysis (SEM FEI Inspect S50) using the free software ImageJ. The powder specific surface areas, pore volumes and average pore sizes were determined by applying the BET and BJH equations to the curve of the N_2 adsorption-desorption isotherms (Micrometric-ASAP 2020). The chemical analyses associated to the sorption experiments were made using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) (Thermo Scientific iCAP 6000 Series). All the pH measurements were realized with F20 FiveEasy Mettler-toledo pH meter.

Strontium extraction

The sorption experiments with strontium ions were conducted in a batch mode. First, the TiO_2 powder was suspended in KOH solution in closed flasks containing the Sr^{2+} aqueous solution. The suspensions were stirred at room temperature, collected at fixed times and filtered. The filtrates were then analysed by ICP-AES to quantify the strontium concentration C_e versus time. The amount of strontium retained on the solid phase, q_e (mg/g), was calculated using equation (1) :

$$q_e = \frac{(C_0 - C_e) \times V}{C_e \times m} \quad (1)$$

where C_o (mg/L) is the initial concentration, C_e (mg/L) is the concentration of each collected sample, m (g) is the TiO_2 mass, and V (L) is the suspension volume. Sorption isotherms for Sr^{2+} have been plotted for a series of TiO_2 powders prepared at 150°C, 250°C and 350°C in SC CO_2 media. Experiments were carried out with TiO_2 suspensions containing 0.2 g/L TiO_2 at different strontium concentration in a range 1-30 ppm. These suspensions were prepared by dilution from a strontium nitrate stock solution (10^{-3} mol/L). The pH was adjusted to a value of 11 with KOH (1 M solution) under N_2 bubbling, in order to avoid any precipitation of strontium carbonate by reaction between strontium ions and atmospheric CO_2.

RESULTS

Powder textural and structural characteristics

The XRD patterns of #DT150, #DT250 and #DT350 samples are given in Figure 1. Only the TiO_2 anatase phase was detected in the samples. The average crystallite size was estimated from the peak width, by applying the Scherrer formula to the (101) XRD peak. The synthesis method thus allows the preparation of anatase nanocrystals with average sizes in the range 5-17 nm (Table 1).

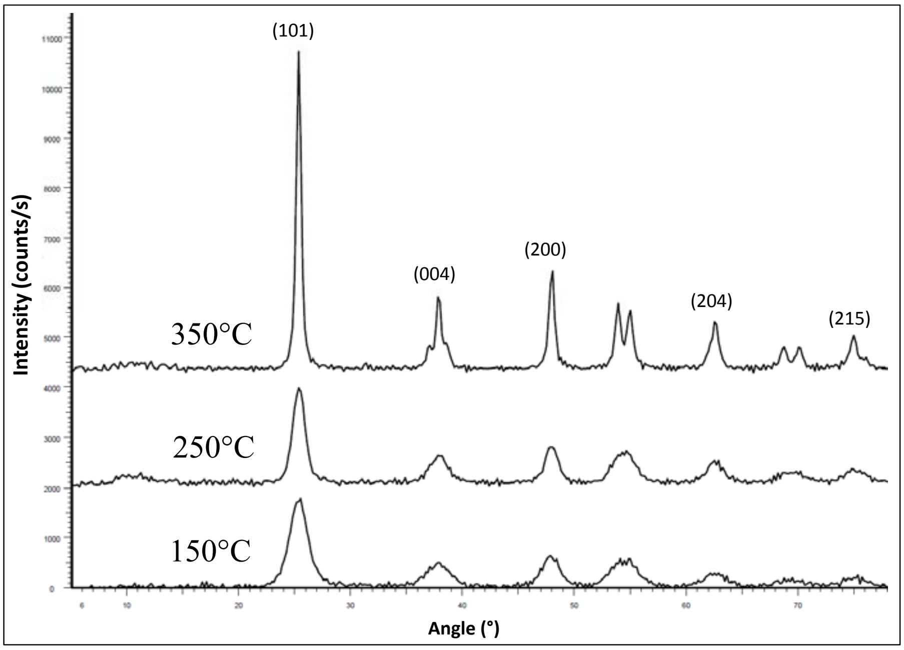

Figure 1: XRD patterns of the TiO_2 powders prepared in SC CO_2 media at 150°C, 250°C, 350°C.

Table 1: Textural properties of the TiO_2 microspheres prepared in CO_2 SC
(Φp: pore diameter; Vp: pore volume, d: crystallite size)

Samples	S_{BET} m^2/g	Φp (BJH) nm	Vp (BJH) cm^3/g	d (XRD) nm	d (TEM) nm
DT150	275	4	0.44	6	5
DT250	192	7	0.54	7	7
DT350	94	14	0.36	13	18

The SEM micrographs presented in Figure 2a show the agglomerated TiO_2 particles and their spherical shape. Average particle sizes are typically micrometric as estimated from the SEM pictures.

Detailed FESEM observations of the TiO_2 particles (Figures 2c and 2d) revealed that the microspheres are porous and composed of aggregated nanosized particles. TEM observations of these nanosized particles (Figure 2b) revealed that they consist of agglomerated TiO_2 nanocrystals. These nanocrystals look rather spherical with average sizes in the range 5-18 nm depending on the synthesis temperature (Table 1). These values are in good agreement with the anatase crystallite sizes derived from XRD patterns.

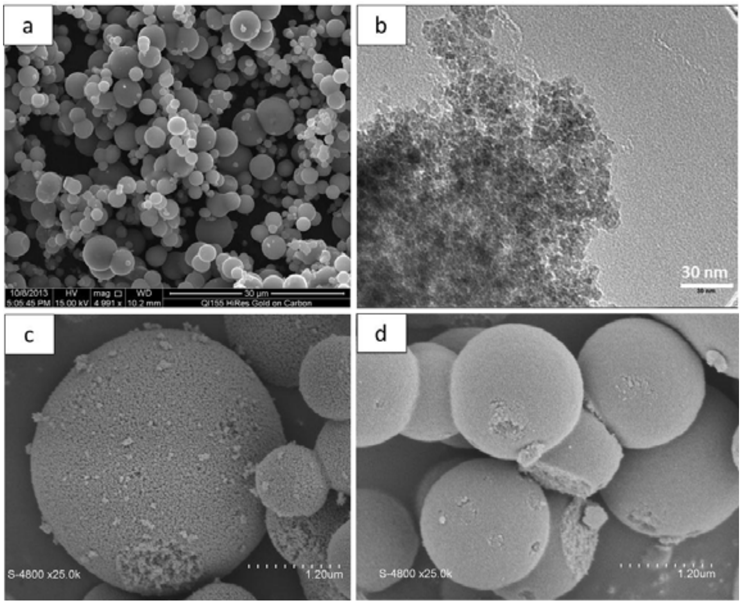

Figure 2: SEM and FE-SEM observations of TiO_2 microspheres prepared in SC CO_2 media at 350°C (a, c) and 150°C (d); and TEM micrographs for TiO_2 nanocrystals produced at 150 °C (b).

N_2 adsorption-desorption isotherms have shown that powders are mesoporous. A summary of the results derived from the N_2 adsorption-desorption isotherms, applying the BET and BJH equations, are given in Table 1. The reaction temperature clearly impacts on the specific surface area, pore size and pore volume. The powder prepared at 150°C, whose specific area reaches 275 m^2/g, has the most promising textural properties for the radionuclide extraction by sorption.

Determination of strontium extraction capacity

The maximum sorption capacity of both the TiO_2 powders synthesized in SC CO_2 and the commercial P25 Degussa powder are compared in Figure 3. The maximum amounts of strontium retained on the #DT350, #DT250, #DT150 and P25-Degussa powders are respectively 17, 41, 62 and 13 mg/g. Obviously the SC CO_2 derived powders have higher sorption capacities than the P25 Degussa sample. This result is attributed both to the higher specific surface area of the powders prepared in SC CO_2 media and to the accessibility of their mesoporous structure. Indeed, the powder textural properties strongly impact on their sorption performances. As expected the #DT150 powder which has the highest specific area gives the maximum sorption capacity.

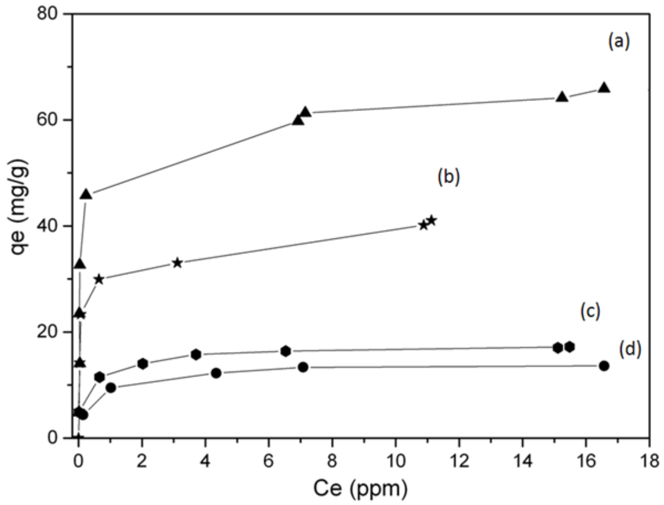

Figure 3: Strontium sorption isotherms of TiO_2 powders: (a) #DT150, (b) #DT250, (c) #DT350 and (d) P25 Degussa.

CONCLUSION

This thermal decomposition of titanium isopropoxide in SC CO_2 media allows direct formation of dry TiO_2 nanostructured powders with a multiscale structure and high surface specific area (> 90 m2/g). The textural characteristics of the powders are key parameters for the sorption of radioactive species in liquid effluents and can be controlled by varying the synthesis temperature in SC CO_2. Actually, the SC CO_2 derived powders revealed a higher strontium sorption capacity than the commercial P25 Degussa powder. The highest performance was obtained for the #DT150 TiO_2 powder (highest specific surface area and highly accessible mesoporous volume) which seems to be the best candidate for the sorption of radionuclides in liquid wastes.

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