Nuclear Instruments and Methods in Physics Research B 411 (2017) 72–77

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Small-angle X-ray scattering (SAXS) studies of the structure of mesoporous silicas

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ARTICLE INFO

Article history:
Received 19 September 2016
Received in revised form 27 January 2017
Accepted 6 March 2017
Available online 13 March 2017

Keywords:
X-ray scattering
SAXS
Mesoporous
Silica
Noble metals

ABSTRACT

Mesoporous ordered silica nanostructures show strong interaction with X-ray radiation in the range of small-angles. Small-angle X-ray scattering (SAXS) measurements based on the elastically scattered X-rays are important in analysis of condensed matter. In the case of mesoporous silica materials SAXS technique provides information on the distribution of electron density in the mesoporous material, in particular describing their structure and size of the unit cell as well as type of ordered structure and finally their parameters. The characterization of nanopowder materials, nanocomposites and porous materials by Small-Angle X-ray Scattering seems to be valuable and useful. In presented work, the SAXS investigation of structures from the group of mesoporous ordered silicates was performed. This work has an objective to prepare functional materials modified by noble metal ions and nanoparticles and using the small-angle X-ray scattering to illustrate their properties. We report the new procedure for describing mesoporous materials belonging to SBA-15 and MCM-41 family modified by platinum, palladium and silver nanoparticles, based on detailed analysis of characteristic peaks in the small-angle range of X-ray scattering. This procedure allows to obtained the most useful parameters for mesoporous materials characterization and their successfully compare with experimental measurements reducing the time and material consumption with good precision for particles and pores with a size below 10 nm.

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1. Introduction

Nanotechnology and new materials with exceptional structure and properties undoubtedly reveal the tendency in actual researches [1–5]. The application of such nanomaterials requires the detailed characterization of nanostructures as well as matching properties to a specific applications. In this connection, the nanoscale porous material should be considered as important binder which linked the traditional silicon derivatives materials and new functional materials obtained by specific treatments and modification with nanometer dimension [6,7]. During last two decades the interest for nanoporous silica materials increased due to advantages that these materials could provide [8–13].

Porous solids are made from a large number of voids which, irrespective of their volume and shapes are referred as pores. Individual pores are separated from each other by solid skeleton, so accordingly, in porous materials we can distinguish area with various electron density. The porosity is a characteristic feature for materials with different composition and structure, both organic, inorganic and hybrid materials as well as materials with or without structural ordering [14] Due to the existence of specific curving of the surfaces in porous materials the increasing of adsorption potential phenomena is observed. Among them, the mesoporous ordered silica materials etched into nanotechnology as an important element with exceptional properties of regular porous structure, high surface area and possibility of surface modification. The synthesis procedure was optimized for many years and involves hydrolysis of the tetraethyl orthosilicate precursor and condensation of their products in the presence of surfactants as compounds with natural ability to self-assembly [15–16]. The structure of mesoporous materials is primarily determined by the type of organic matrix as a scaffolding, synthesis conditions and interaction between organic and inorganic components. In the family of ordered mesoporous silicates, the materials labeled as SBA-15 (Santa Barbara Amorphous) and MCM-41 (Mobile Crystalline Material) seem to have the greatest application significance. SBA-15 structures are the two-dimensional hexagonal materials (p6mm) prepared using block copolymer PEO/PPO/PEO with block ratio of 20/70/20 or cetyltrimethylammonium bromide (CTAB) surfactant in the case of SBA-15 and MCM-41 respectively. They are

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http://dx.doi.org/10.1016/j.nimb.2017.03.028
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characterized by a narrow pore diameter distribution (2–10 nm) thick structure of the walls (approx. 3–6 nm). This last feature for SA-15 is responsible for relatively high thermal and hydrothermal stability. Although the two types of materials SBA-15 and MCM-41 have the same hexagonal symmetry, the significant difference is observed in relation to the existing micropores. SBA-15 materials contain a large number of micropores combining individual mesopores which are generated during the synthesis. The micropores situated around a cylindrical form of mesopores forming the specific microporous crown. In this area, lower density of the material within the mesopores compared with pure silica material were occurred [17]. Specific properties of porous materials them an excellent catalyst carriers. In this instance, metal nanoparticles, in particular nanoparticles of noble metals, deposited on solid surface form the highly dispersed metal phase and important element in many industrial processes [18–19]. Such small size causes the appearance of unprecedented features and capability. Due to the small size nanoparticles are subject not only in classical physics embrace, but also important part of quantum physics [20]. The small size allow to overcome the biological barriers and make such materials biocompatible what is important in precise medicine applications.

In this instance, materials based on the mesoporous ordered support modified by noble metal nanoparticles were prepared and investigated by Small Angle Scattering of X-rays. It is a fundamental method of analysis the structure of condensed matter and important technique for characterization of porous structures. So far, the pore size, thickness of the pore walls, pore volume and specific surface area were usually defined by combination of gas adsorption/desorption data (nitrogen or argon) [21] or XRD data according KJS method [22,23]. Additionally, studies performed by Pikus et al. [24] have shown the procedure of structural parameters defining of ordered mesoporous materials (OMM) only from SAXS patterns. The contribution of such studies was appreciated by many later works [25,26]. The usefulness of this method has been checked for authors for pure materials MCM-41 and SBA-15. Still are attempts to develop other methods for determining the structural properties of this type of materials. The aim of presented work was verification the procedure of porous structure parameters determination by SAXS method for more complex materials constituting the dispersed metal phases deposited on mesoporous ordered silica materials in the type of MCM-41 and SBA-15.

2. Experimental

2.1. Materials

Self-assembly agent Pluronic P123 composed by blocks of different polymerized monomers (poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) ($EO_{20}PO_{70}EO_{20}$, Mw = 5800) and tetraethyl orthosilicate (TEOS, 98%) as an organic silicon source were purchased from Sigma-Aldrich. Noble metal precursors tetraammineplatinum(II) chloride hydrate ($[Pt(NH_3)_4]Cl_2$, 98%) and tetraamminepalladium(II) chloride monohydrate (proportional content of Pd was provided as 39% min.) were purchased from Sigma-Aldrich and Alfa Aesar GmbH & Co KG (Germany) respectively. Diamminesilver(I) complex $[Ag(NH_3)_2]^+$ was prepared in place from silver nitrate (0.3 mol·L^{-1}), sodium hydroxide (1.25 mol·L^{-1}) and concentrated (25%) ammonium hydroxide for metal ammine complexes formation.

2.2. Materials preparation

The preparation of mesoporous ordered silica materials (SBA-15 and MCM-41) mesophases consisted on the addition of silica source into a polymer or surfactant template as a basis of their internal structure, in acidic or basis solution respectively. Synthesis were carried out at constant temperature for synthesis mixture (35 °C) and aging step (95 °C). For obtaining SBA-15 mesoporous silica the non-ionic polymer Pluronic P123 was dissolved into the solution of 30 mL deionized water and 120 mL of HCl (2 mol·L^{-1}), followed by the addition of 9.12 g of tetraethyl orthosilicate. In the case of MCM-41 samples, cationic surfactant (CTAB (Cetyl trimethylammonium bromide) was used as a template materials. The mixtures were maintained at 35 °C for 24 h under stirring, and heated at 95 °C for 48 h. After synthesis the template was removed by high temperature treatment at 550 °C for 4 h with 3 °C/min heating rate in muffle furnace under an air-atmosphere.

As prepared mesoporous ordered silica phases were modified by noble metal ions and further noble metal nanoparticles by wet impregnation and thermal reduction. In this instance, calcined mesoporous silica was immersed in aqueous solution (10 mL and pH ~ 8.5) containing ammine complexes of noble metals. The mixtures were kept in an ultrasonic bath for 1 h and left overnight without stirring. Products were recovered by filtration and treated from room temperature to 600 °C for reduction of noble metal ions to metallic form. Only AgCl/SBA-15 sample was prepared in different manner described in detailed in our previous work [27].

2.3. Measurements and calculations

The obtained composites were analyzed by X-ray diffraction (XRD) Empyrean diffractometer (PANalytical) with CuKα radiation (λ = 1.5418 Å) in the wide range of 2θ. The SAXS patterns were recorded over a 2θ range of 0.5–5° (q range of 0.035–0.36 $Å^{-1}$ where q as scattering vector is defined as $q = (4\pi \cdot \sin\theta)/\lambda$). The background subtraction from proper SAXS curve was performed by WAXSFIT [28] software using all range of measured scattering vector, to obtain the accurate intensity of (1 1 0) and (2 0 0) signals. Transmission electron microscopy (TEM) was carried out on a high resolution scanning transmission electron microscope Titan G2 60-300 (FEI). The N_2 adsorption/desorption isotherms were obtained at −196 °C over the full range of relative pressures, using a Micromeritics ASAP2020 equipment. Specific surface areas were computed from experimental isotherms by applying the BET theory. Data analysis was performed using MicroActive software (Micromeritics). Mesopore pore-size distribution curves were obtained from the desorption branch of isotherm using the Barrett-Joyner-Halenda (BJH) model with cylindrical pores and Faas correction without smooth differentials. [29]. All samples were outgassed before analysis at 120 °C for 24 h in degas port of analyzer.

3. Results and discussion

In small-angle X-ray scattering measurements the angle of scattering (2θ) can be less than 5°. This allows the evaluation of structures in the nanometer scale. In this study, the original procedure for mesopores widths determination were proposed and applied for describing the properties of mesoporous silicates modified by highly dispersed noble metal phase (Fig. 1D). The type of the pores ordering can be described as cylindrical channels (hexagonality parameter = 0) and hexagonal channels (hexagonality parameter = 1) for SBA-15 and MCM-41 materials respectively. Fig. 1A and B shows schematically illustration of both models. We suggest that intensity of second peak indexed as (1 1 0) depends particularly on the ratio of the pore diameter to the unit cell. Additionally their sensitivity to any changes of pore size are enhanced in comparison to the (1 0 0) peak which high intensity and position in the range of the lowest angle generate some errors

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