Use of Supercritical Carbon Dioxide for Direct Preparation of Crystalline Monolithic TiO2 Aerogels.

Cerhová, Marie
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M. Cerhová, M. Sajfrtová, [1]L. Matějová, V. Dřínek, [2]S. Daniš, V. Jandová
Institute of Chemical Process Fundamentals of the ACS, v.v.i., Rozvojová 135, 165 02 Prague 6, Czech Republic, sajfrtova@icpf.cas.cz; [1]Institute of Environmental Technology, VŠB-Technical University of Ostrava, 17.listopadu 15/2172, 708 33 Ostrava – Poruba, Czech Republic; [2]Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University in Prague, Ke Karlovu 5, 121 16 Prague 2, Czech Republic

Titania aerogels are special highly-porous materials often used in the form of monoliths [1]. Their very high specific surface area makes them attractive candidates in many applications: solar energy conversion [2], photocatalysis [3], electronic devices [4], or as supporting material in the catalytic reactions [5]. The (photo)catalytic activity of monoliths critically depends on the structural properties such as crystal phase composition and crystallite size. Crystalline and pure TiO_2 aerogels are commonly prepared by calcination. However, this thermal treatment results in uncontrollable destruction of porous structure of titania aerogels, commonly accompanied by the decrease of the surface area as well as the porosity [6]. Therefore, gentler methods for the preparation of TiO_2 aerogels are desirable to optimize their morphology and functionality. Use of supercritical carbon dioxide ($scCO_2$) seems to be perspective way to obtain crystalline and pure TiO_2 monoliths without any subsequent thermal treatment [7, 8].

The present work deals with the crystallization of monolithic TiO_2 aerogels in environment of pure and water modified $scCO_2$. To remove organic precursors used during sol-gel synthesis and to crystallize TiO_2 the combination of several steps with pure and water-modified $scCO_2$ was tested with respect the high porosity and the specific surface area of titania blocks.

The effect of temperature (40-100 °C) and water concentration in $scCO_2$ (5-30 wt. %) on structural and textural properties was investigated at constant pressure of 30 MPa. The structural properties of the prepared monolithic TiO_2 were characterized by Raman spectroscopy. The textural properties such as specific surface area, content of mesoporous and volume of microporous were determined from nitrogen physisorption and skeletal density by helium pycnometry measurements.

The pure $scCO_2$ caused any crystallization. When 5 or 15 wt. % of water was added as a $scCO_2$ modifier a crystalline structure was obtained. The specific surface areas of mesoporous titania changed between 200-634 m^2/g. Increasing the temperature and the concentration of water in $scCO_2$ resulted into the decrease of specific surface areas and change of the monoliths into the more fragile blocks.

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