Use of Water- And Ethanol-Modified Supercritical Carbon Dioxide for Direct Preparation of Crystalline Monolithic TiO2 Aerogels.

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USE OF WATER- AND ETHANOL-MODIFIED SUPERCRITICAL CARBON DIOXIDE FOR DIRECT PREPARATION OF CRYSTALLINE MONOLITHIC TiO_2 AEROGELS

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TiO_2 forms three crystalline phases (anatase, brookite, rutile), of which anatase is the most investigated because of its high photocatalytic activity. Due to its chemical stability, strong oxidation activity and non-toxicity, anatase is used especially for air- and water-purification [1]. Titania aerogels in the monolithic form has been extensively applied for the various applications such as solar energy conversion [2] and photocatalysis [3]. The use of TiO_2 for a given application depends not only on the phase composition, but also on specific surface area, crystallinity and crystallite-size. These properties can be significantly influenced by the preparation method used.

Crystalline and pure TiO_2 aerogels are commonly prepared by calcination accompanied by the uncontrollable porous structure destruction, decrease of surface area as well as porosity [4] and also the photocatalytic performance cannot be easily managed. As a perspective way to obtain crystalline and pure TiO_2 monoliths without any subsequent thermal treatment seems to be the using of supercritical carbon dioxide ($scCO_2$) [5, 6]. With this gentle method can be the structural, textural and physicochemical properties better controlled.

We studied a combination of supercritical CO_2, water and ethanol for the preparation of crystalline and pure nanostructured TiO_2 without any thermal processing. The effect of temperature (40-150 °C) and sequence on structural and textural properties was investigated at constant pressure of 30 MPa. The prepared aerogels were characterized with respect to the (micro)structural properties by Raman spectroscopy and X-ray diffraction. 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 ethanol-modified $scCO_2$ caused any crystallization. However, when as the subsequent step water-modified CO_2 was added the crystallization to anatase and brookite structure was reached. The specific surface areas of mesoporous titania changed between 240-660 m^2/g. Increasing the temperature resulted into the decrease of specific surface areas, change of the monoliths colour from white to yellow and into the more fragile blocks.

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