Influence of Water-Ethanol-Modified Supercritical Carbon Dioxide at the Preparation of Crystalline Monolithic TiO2 Aerogels.

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Influence of water-ethanol-modified supercritical carbon dioxide at the 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. In our previous studies [7-9], the efficiency of this method was demonstrated for TiO_2 in the forms of thin films and aerogels in which water and ethanol were used as modifiers. The critical effect of water on the TiO_2 crystallization and the beneficial influence of ethanol on the purity and phase composition of TiO_2 were found.

This work is focused on a study of TiO_2 aerogel SFC with $scCO_2$ modified by mixture of ethanol and water in a ratio 1:1. The effect of temperature (40-100 °C), pressure (10-30 MPa) and modifier concentration in $scCO_2$ (5-15 wt.%) and the additional drying with pure CO_2 on microstructure, purity and textural properties of TiO_2 aerogel was investigated. Processed monoliths were characterized by XRD analysis, Raman spectroscopy and N_2 physisorption.

Increasing temperature, pressure or modifier concentration in $scCO_2$ showed the positive effect on the aerogel purity. However, the temperature of 100 °C or the presence of too large amount of mixture (i.e. 15 wt.%) resulted into the aerogel destruction. The specific surface areas of mesoporous titania changed between 222-498 m^2/g. Increasing the pressure and temperature resulted into the decrease of monolith specific surface areas, change of the monoliths colour from white to yellow and into the more fragile blocks.

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