

Studies on preparation of mesoporous oxide materials Based on The Sol-gel Process

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The mesoporous metal oxides are an important class of materials, because the surface area/volume ratio of a material is increased by manyfold, making them very useful in surface-related applications. The physical properties of the mesoporous titania can be improved by controlling its particle size in nano-scale and stabilizing the microstructure via supercritical drying, surface modification, suppression of grain growth with addition of the second oxide such as silica and alumina, and sulfation of surface. The CO₂ supercritical extraction technique will provide a new route to obtain mesoporous anatase consisting of nanoparticles, less than 10 nm in diameter, at low temperatures. The fractal analysis using N₂ adsorption isotherm makes it possible to evaluate surface morphology in nanometer scale. Surfactants are also used to modify the porous structure of gels. Adsorption of cationic surfactants of BTAC and CTAC into pores is controlled by hydrophobic interactions. Surfactant tail-groups will interact with any hydrophobic regions that are present on the pores of the gel network. The surfactant component can be removed by combustion to obtain pores. However, the pore size, depending on the surfactant species, is much smaller than the supercritically extracted gel.

Anatase was stabilized by suppression of grain growth with sulfation and silica addition. Mesoporous powders with high porosity and large surface area were obtained by the supercritical extraction of the wet gels with CO₂. The porous structure of the sulfated anatase aerogel obtained in this work is thermally more stable than the un-sulfated aerogel. The sulfate phase, bridged bidentate Ti₂SO₄ on the surface of anatase restrains the grain growth of anatase, and retards the phase transformation from anatase to rutile. Also, with addition of a large amount of SiO₂, the grain growth rate of crystalline TiO₂, anatase, is restricted, and anatase phase is thermally stabilized.

The phase transformation sequences as functions of temperature are as the followings. (1) The anatase titania phase of the as-extracted gel is stable after calcinations at temperatures up to 500°C, the anatase then begins to transform into rutile at 600°C, and finally, the anatase phase completely transforms into rutile at 700°C. (2) The anatase phase is found for the amorphous sulfated titania after calcination at 500°C, the anatase is stable up to 700°C, and begins to transform into rutile at 750°C, and finally, only rutile phase is found after calcination at 800°C. (3)

At temperatures up to 1000°C, no phase transformation of anatase to rutile is observed for the $\text{TiO}_2 \cdot 2\text{SiO}_2$ aerogel. (4) The titania-alumina aerogel is amorphous at temperatures up to 800°C, and rutile directly deposits at 800°C. On the other hand, anatase phase of as-extracted sulfated titania-alumina aerogel is stable after calcination at temperatures up to 900°C and begins to transform into rutile at 1000°C.

The effects of additives, silica and alumina, on the thermal evolution of titania aerogels are different. The grain growth of anatase is restricted with addition of SiO_2 . Anatase nanoparticles in the $\text{TiO}_2 \cdot 2\text{SiO}_2$ aerogel are surrounded with SiO_2 nanoparticles and highly dispersed, thus, the grain growth rate is low. Also, a large amount of SiO_2 will retard the crystallization of TiO_2 and the phase transition from anatase to rutile. This event is probably due to the small particle size of anatase. The alumina-titania gels calcined at 750°C or lower temperatures were amorphous without nucleation of anatase. The amorphous network of alumina-titania gel that consists of heterometal-oxygen bonds may be strongly hydroxylated and stable. The decomposition of the stable amorphous phase occurs at 800°C resulting in direct deposition of rutile phase. Both of the additives induced larger porosity and larger surface area.

Acidity of titania can be improved by formation of bridged bidentate, Ti_2SO_4 , on sulfation and formation of hetero metal-oxygen bonds. It appears that solid superacids promote the esterification of free fatty acids. Sulfated titania (SO_4/TiO_2) and sulfated titania-alumina ($\text{SO}_4/\text{TiO}_2\text{-Al}_2\text{O}_3$) are typical examples of these superacids and exhibit high catalytic activities for various reactions. Catalytic activity is closely correlated to the acidity of catalysts. Namely, the higher acidity, the higher is catalytic activity. Activity of titania as catalyst for esterification can be improved by sulfation on the surface and increases in the porosity and surface area. It is expected that its acidity and porosity would be enhanced and that its catalytic activity towards the esterification, especially in the esterification of long chain carboxylic acid (fatty acid), would be improved. These techniques, sulfation and formation of hetero-metal-oxygen bonding through the sol-gel reaction, are not complex and they can be performed using a standard apparatus, so that they are easily applied to prepare useful oxide materials.