Nanocrystalline Mesoporous Titania Catalysts for the selective oxidation of benzyl alcohol to benzaldehyde

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Introduction

Evaporation-Induced Self-Assembly (EISA) is a powerful and well-suited approach to design functional mesoporous oxides with fine tuned structural, compositional and morphological properties [1]. This method relies in using soluble inorganic species with very dilute surfactant initial concentration from which a liquid crystalline mesophase is gradually developed upon solvent evaporation. The initial inorganic framework is not fully condensed allowing the control of the final mesostructure by modifying processing conditions. This transition state is known as modulable steady state (MSS) [2]. Then, the slow co-assembly between the inorganic network and liquid crystalline phase leads to long-range order-well defined mesostructures.

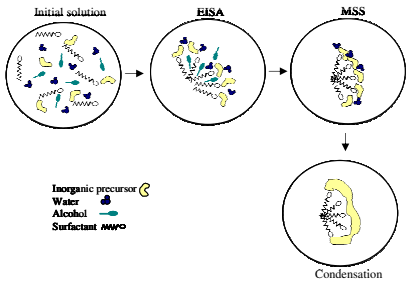

Figure 1. *Schematic representation of EISA*

In particular, TiO_2 possessing very interesting catalytic, photochemical, and electrical properties [3], represents an attractive system for mesostructuring via EISA. Herein we report the successful synthesis of mesostructured nanocrystalline TiO_2 by EISA. Processing parameters, such as relative humidity and aging temperature, as well as chemical parameters such as relative amounts of ionic and non-ionic surfactants were explored. The resultant ordered mesophases displaying uniform anatase nanocrystals, with high surface areas and unimodal pore size distribution were employed as *porous nano-catalysts* for the oxidation of benzyl alcohol to benzaldehyde.

Materials and Methods

Mesoporous nanocrystalline TiO_2 was prepared under mild synthesis conditions by reacting aqueous solution of Titanium Butoxide with the structure directing agent CTAB. In a typical synthesis, the inorganic precursor was dissolved in ethanol or 1-butanol. The solution was vigorously stirred until the precursor was dissolved completely. Then, a CTAB-alcohol solution was added dropwise to the precursor solution under continuous stirring for about 30 min. The gel was then transferred to a petri dish and aged at T = 20ºC, RH = 60 %. The gel was completely dried at 60ºC for 24 h. The surfactant was removed by calcination in air at 350ºC-450ºC for 6 h to yield the mesoporous nanocrystalline anatase. BET surface area, N_2 adsorption-desorption isotherms were determined using a Tristar-3000 micromeritics porosimeter. The crystalline structure was determined by XRD diffraction using Rigaku DMAX B and FEG-TEM/STEM. Catalytic test were carried out in a 0.1 dm^3 tank reactor under UV radiation at room temperature and atmospheric pressure.

Results and Discussion

We successfully prepared mesoporous nanocrystalline TiO_2 by EISA. CTAB, a cationic surfactant was used as the structure directing agent to direct the synthesis. The resultant mesophases displayed surface areas in the ~70-110 m^2/g range, with unimodal mesopore sizes in the ~2-10 nm range. Figure 2 shows a typical adsorption-desorption isotherm of a synthesized sample displaying the characteristic type IV isotherm of mesoporous materials, and unimodal pore size distribution ~4.5nm. Interestingly, the walls of the mesostructure were composed of ~8 nm anatase crystals (Figure 3). XRD (not shown here) confirmed the crystalline nature of the wall structure. Preliminary catalytic data shows that these mesophases displayed superior catalytic performance for the oxidation of benzyl alcohol to benzaldehyde as compared to Degussa P-25 catalyst. The enhanced catalytic performance of the synthesized mesophases is not only because of textural and structural advantages such as larger surface areas, unimodal pore sizes and mesoporous architectures of the mesophases, but also because of the presence of small anatase nanocrystals.

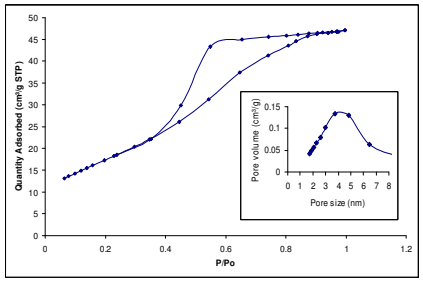

Figure 2. *N_2 adsorption-desorption isotherms and pore size distribution of mesoporous nanocrystalline TiO_2*

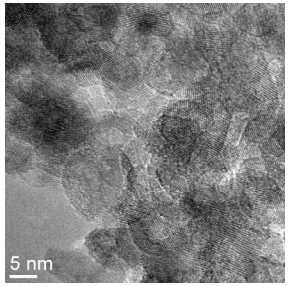

Figure 3. *TEM of mesoporous TiO_2 showing anatase nanocrystals*

Significance

Herein we have reported the successful synthesis of nanocrystalline mesoporous titania with unimodal pore sizes in the ~ 2-10nm range, surface areas as high as 110 m^2/g and displaying the catalytically active and selective anatase phase for the oxidation of benzyl alcohol to benzaldehyde. These novel mesophases displayed superior catalytic performance as compared to the commercial Degussa P-25 catalyst.

References

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