High Surface Area ZnO Nanoparticles via a Novel Continuous Precipitation Route**

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High surface area ZnO nanoparticles are synthesized by applying a novel continuous precipitation method using a micromixer coupled directly to a bench-top spray dryer. The polycrystalline material is obtained by fast turbulent precipitation from aqueous zinc nitrate solutions with either sodium or potassium carbonate followed by immediate quenching of the aging due to the rapid water removal. Specific surface areas up to 98 m² g⁻¹ are obtained, depending on the precipitant and the sequence of unit operations applied after precipitation.

1. Introduction

Zinc oxide is an interesting material for a wide range of applications due to its unique electronic and optical properties.¹ It is a wide-gap semiconductor that is also luminescent, thus being a promising candidate for optoelectronic applications. Because of the good conductivity and high transparency in the visible region, thin films of ZnO² have been investigated as transparent electrodes for solar cells.³ Furthermore, zinc oxide nanoparticles have been used as white pigment⁴ or as gas sensors,⁵ for example, for detection of hydrogen⁶ or nitrogen oxide gases.⁷

Metal oxides used as supports or active components play an important role in catalytic reactions. Industrial oxide supports are mainly produced by precipitation from aqueous solution or by gelation of a hydrophilic colloidal solution.⁸ Small particles are generally favored, and the synthesis method should provide control over the surface area, the pore volume, and the pore size distribution of the material. Of particular interest is the application of ZnO as a component of composite catalysts, for instance for methanol synthesis. When the high-pressure high-temperature methanol synthesis was introduced by BASF in 1923,⁹ it was conducted over a catalyst consisting of zinc oxide and chromia. Since 1966, methanol synthesis has been catalyzed by a ternary Cu/ZnO/Al₂O₃ system, providing the possibility to reduce the pressure and the temperature of the process. It is generally accepted that a large Cu surface area leads to increased catalytic performance,¹⁰ and recent studies emphasize the importance of the Cu/ZnO interface.¹¹,¹² Methanol synthesis over Cu-free ZnO occurs at a much lower rate.¹³,¹⁴

The industrial production of nanoscale ZnO particles is mainly based on the oxidation of Zn vapor. Therefore, either metallic Zn is evaporated followed by an exposure to oxygen or Zn-containing material is reduced with carbon and subsequently re-oxidized.¹⁴ About 1–2% of the industrially used ZnO is generated using wet chemical methods such as precipitation of zinc hydroxides or carbonates, e.g., from aqueous solutions of ZnCl₂, ZnSO₄, or Zn(NO₃)₂ followed by washing and calcination. Commonly used pyrogenic materials usually have a specific surface area of around 20 m² g⁻¹. It is reported that NanoTek-ZnO has a surface area of 18 m² g⁻¹,¹⁵ whereas VP AdNano-ZnO 20 has 20–25 m² g⁻¹.¹⁶ Wet chemical preparation is generally chosen to obtain ZnO materials with larger specific surface areas, for example 48 m² g⁻¹.¹⁷ The thermolysis of a volatile organometallic zinc siloxide precursor resulted in a specific surface area of 153 m² g⁻¹,¹⁸ and recently hierarchically structured ZnO was prepared by solvothermal synthesis using zinc foils in aqueous EDA solution with specific surface areas up to 186 m² g⁻¹.¹⁹ By using a hard-matter carbon template, ordered mesoporous ZnO materials with about 200 m² g⁻¹ were synthesized.²⁰ However, the space-time yield of these methods is considered rather low.

The precipitation of large quantities of material in a batch procedure is not a well-defined process. Even if the precipitation conditions are kept constant, the chemical potential of the

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