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Oxides in catalysis: Role of reducibility from biomass conversion to CO oxidation

Gianfranco Pacchioni

Università di Milano-Bicocca, Italy

Reduced oxide supports often exhibit a higher catalytic activity than the stoichiometric surface. Examples are production of liquid fuels from lignocellulose or CO oxidation to CO₂. Despite the very different reactions, the catalysts are similar: Ru/TiO₂ and Ru/ZrO₂ in biomass conversion and Au/TiO₂ and Au/ZrO₂ in CO oxidation. The common denominator is that removing oxygen from the oxide surface, with formation of oxygen vacancies, results in enhanced catalytic activity. The reasons are clearly identified by studying, with a density functional theory approach, the profile for the reactions where a reduced surface gives lower barriers. However, while TiO₂ is a reducible oxide, ZrO₂ is not, at least if based on measures of bulk reducibility. We will show that several mechanism, in particular nano-structuring and formation of metal/oxide interfaces can drastically change the surface chemistry of an oxide making zirconia reducible and as active as titania in catalysis by oxides.

gianfranco.pacchioni@unimib.it

Acoustic-chemical synthesis of nanosized BaTiO₃ and its dielectric response

Hatice Zehra Akbas

Mustafa Kemal University, Turkey

Ultrasonication is an advanced process used to obtain sub-micron size powders because the collapsing of bubbles creates hot spots with about 5000 K and 1000 atm pressure in the liquid, which separates the particles from each other during the process. Ultrasonication has been used successively for deagglomeration, degassing, and homogenization for a decade. Crystallize phase of BaTiO₃ ceramics that ultrasonication method used to homogenize and deagglomerize the reagents were better than the ceramics using a mechanical method after the solid-state reaction. The structure of samples without carbonate impurities was verified using Fourier transform infrared spectroscopy (FT-IR) and X-ray diffractometer (XRD). Scanning electron microscopy (SEM) analysis of the powders showed that using ultrasonic deagglomeration greatly decreased the particle size with perfect homogeneity in the shortest time. The particle size of the powders was calculated as 44.7 and 80.4 nm for ultrasonic and mechanochemical deagglomeration, respectively. The sintered pellet from the ultrasonic method had no abnormal grain growth, and the grain sizes were between 10-30 μm. The pellet from the mechanical method had an abnormal grain growth, and the grain sizes were between 10-100 μm. The complex permittivity (ε' and ε'') and the AC conductivity (σ') of the samples were analyzed in a wide frequency range of 20 Hz-2 MHz at room temperature. Using acoustic method reduced ε' a little but decreased ε'' that well enough. The method can make a significant improvement to produce high purity homogeneous BaTiO₃ ceramics without carbonate impurities with a small dielectric loss.

hatice-akbas@windowslive.com