

Shape and Pore Size Controlled Scalable Synthesis of Functional Oxide Nanostructures through Exothermic Chemical Reactions

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Abstract:

Mesoporous metal oxides with uniform shape and porosity are of considerable interest. Their economical production at a large scale in an efficient manner, however, still remains a challenging task for commercialization. We report for the first time a scalable, economic, energy and time efficient method for the synthesis of crystalline mesoporous oxide catalysts (Cr_2O_3 , CeO_2) with tailored shape and porosity, by utilizing exothermic chemical reactions (Figure 1). In contrast to wet methods, such as hydrothermal synthesis (e.g. soft or hard templates method) which takes hours to proceed in a constant temperature and constant volume reactor, exothermic reactions has rapid thermal and mass transfer processes. The high temperature required for crystal nucleation is achieved by the self-generated heat. Rapid cooling (typically few seconds) does not provide sufficient time for extended crystal growth, leading to nanoscale crystals. By carefully controlling the synthesis conditions metal oxides with uniform shape, uniform porosity, high specific surface area, high pore volume and high crystallinity can be fabricated. As-prepared mesoporous CeO_2 possesses uniform 22 nm pores, 0.6 ml/g pore volume, which is the highest pore volume for CeO_2 reported. The porosity estimated from pore volume of 0.6 ml/g and CeO_2 density (7.28 g/ml) is 81%, which is higher than the theoretical limit (74%) of closed packed spherical cavities. The additional porosity above the closed packed spheres limit may come from micropores between the CeO_2 nanocrystals since the measured micropore volume is 0.075 ml/g, which is equivalent to 12.5% porosity. The estimated porosity of 81% approaches the value (>90%) of common aerogels which are open frameworks formed by networked nanoparticles. We used combination of different characterization techniques to understand the mechanistic details of the process.

The obtained mesoporous CeO_2 catalyst exhibited excellent catalytic activity for soot and carbon monoxide oxidation. In principle this method can be applied to synthesize different high porosity

crystalline metal oxides (binary, ternary). Large scale production of CeO_2 has been demonstrated by 0.5 kg ceria-3 catalyst produced within five hours.

Keywords: exothermic reactions, nanoporous oxides, ceria, heat transfer, catalytic applications, oxidation,

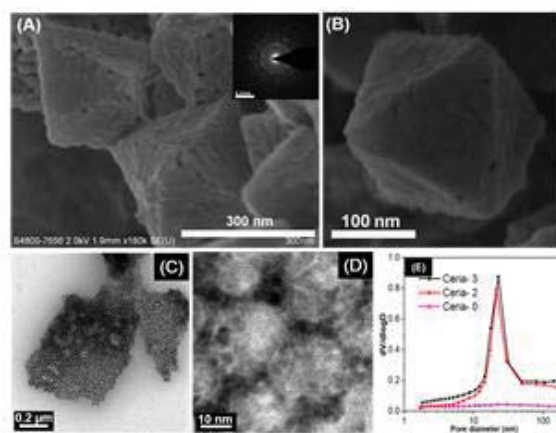


Figure 1: SEM images of Cr_2O_3 octahedra (A, B), TEM images of CeO_2 catalyst (C, D) and BJH pore size distribution plots of CeO_2 catalysts prepared through exothermic chemical reactions.

References:

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