



The prevalence of surface oxygen vacancies over the mobility of bulk oxygen in nanostructured ceria for the total toluene oxidation



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ABSTRACT

This paper reveals the key importance of surface oxygen defects in the oxidation catalytic activity of nanostructured ceria. A series of nanostructured rods and cubes with different physico-chemical properties have been synthesized, characterized and tested in the total toluene oxidation. The variation of the temperature and base concentration during the hydrothermal syntheses of nanostructured ceria leads not only to different ceria morphologies with high shape purity, but also to structures with tuneable surface areas and defect concentrations. Ceria nanorods present a higher surface area and a higher concentration of bulk and surface defects than nanocubes associated with their exposed crystal planes, leading to high oxidation activities. However, for a given morphology, the catalytic activity for toluene oxidation is directly related to the concentration of surface oxygen defects and not the overall concentration of oxygen vacancies as previously believed.

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1. Introduction

Ceria-based materials have been intensively studied in the catalysis field, either as pure dioxide (CeO₂) or doped materials, due to its high abundance and desirable combination of chemical and physical properties [1,2]. Especially, ceria-containing oxides have been researched and employed in a wide range of catalytic applications including the three-way catalytic system for exhaust gases [3], water gas shift reaction [4], VOC oxidation [5], steam reforming of alcohols [6], photocatalysis [7] and electrocatalysis [8] among others. In the recent years, research has focused on the understanding of the properties of nanostructured ceria as a way of tuning and further improving its redox activity, surface to volume ratio and

oxygen storage capacity [9–12]. The catalytic activity of nanostructured ceria is strongly related to the exposed surface crystal plane. Computer modeling has shown that surface energy increases on the ceria surfaces from (1 1 1) plane to (1 1 0) < (1 0 0) < (2 1 0) < (3 1 0), the former one being the most stable. Sayle et al. [13] have shown that, theoretically, the (1 0 0) surface plane is catalytically more active than the (1 1 1) and (1 1 0) surfaces and Campbell and Esch [11,14] gave evidence of the surface oxygen vacancies on CeO₂ (1 1 1) being immobile at room temperature while clusters are formed at high temperatures. These theoretical predictions have been experimentally demonstrated in a series of studies. Mai et al. [9] have shown that ceria structures with (1 0 0)/(1 1 0) dominating planes present a higher activity toward the CO oxidation reaction due to their higher lattice oxygen migration from bulk to surface compared to the (1 1 1) dominated ceria. More recently, we have observed a similar trend for the full oxidation of volatile organic compounds [5] in accordance with the enhanced oxygen storage capacity of the (1 0 0) exposed surface [15].

Selective surface plane exposure can be successfully achieved by controlling the morphology of the material at the nanoscale.

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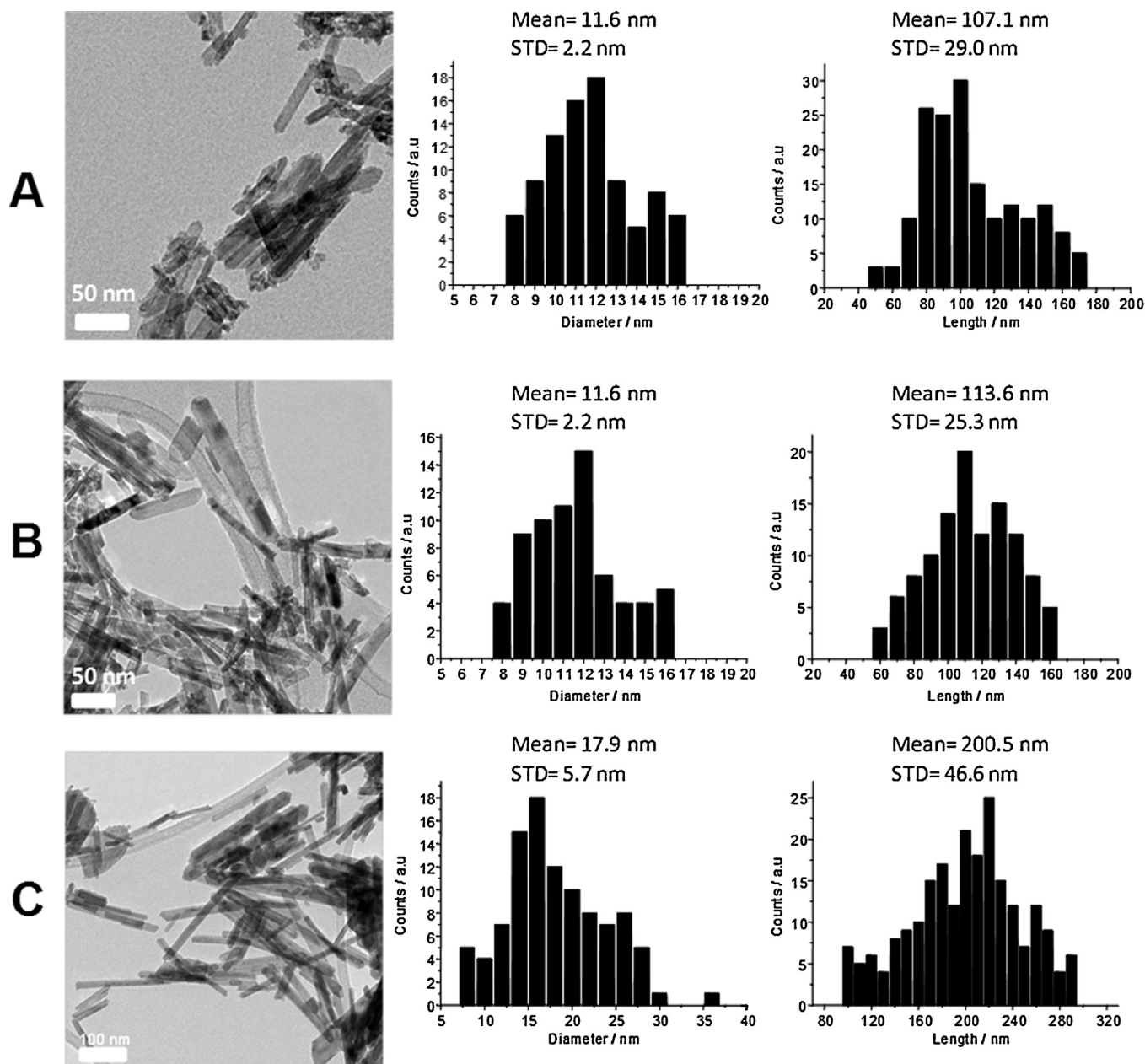


Fig. 1. TEM images and diameter and length histograms of ceria nanorods A) CeO₂_nr.A, B) CeO₂_nr.B and C) CeO₂_nr.C. A minimum of 200 rods were measured for each histogram.

Consequently, a variety of methods have been developed to synthesize nanosized ceria including the use of templates, special organic reagents, hydrothermal treatment, electrochemical methods, etc. [16,17] to form a wide range of morphologies from particles [10], polyhedrons [18], rods [19], tubes [20,21], spheres [6], cubes [22], etc.

Despite the importance of morphology in the final chemical and physical properties of ceria, particle and crystallite size are also believed to play a key role, especially determining its catalytic activity. However, this role is still not fully understood leading to the current debate in the literature. On the one hand, some studies show that the concentration of Ce³⁺ increases as the crystallite size decreases imparting unusual characteristics to the nano-sized material [22–24]. However, Xu et al. [10] claimed that the structural and chemical variations observed in ceria at sizes below 5 nm are due to the strain effect of higher surface energy associated with its lattice expansion with no relation to increasing the Ce³⁺

surface concentration. The oxygen storage capacity of the nano-sized ceria seems to show a clear quantum effect [10], the smaller the particle size, the higher the observed reducibility, in terms of the utilization of surface oxygen [16]. It is important to highlight that particle size does not seem to be directly related to reducibility in zirconium-doped ceria [15]. However, most of these studies refer to particulated ceria and there is still a lack of understanding of the relative dependency of crystallite size and surface and bulk properties to catalytic activity of different ceria morphologies in which different surface planes are selectively exposed. In this paper, we show that crystallite size plays a key role in the reactivity of ceria rods with enclosing (1 1 0) and (1 0 0) facets, while it has the modest effect on the catalytic activity of ceria cubes with exposed (1 0 0) facets. More importantly, we demonstrate that the oxidation catalytic activity of nanostructured ceria shows a linear relationship with the concentration of surface oxygen defects playing a key role in the reaction mechanism, however, the concentration of

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