Surface structure dependence of selective oxidation of ethanol on faceted CeO_2 nanocrystals

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ABSTRACT

Shaped CeO_2 nanoparticles have been used to explore the effect of surface structure upon the surface chemistry and catalytic selectivity for the ethanol selective oxidation reaction. CeO_2 octahedra, cubes, and rods were synthesized using previously published methods. Adsorption and desorption behavior on these nanoshapes was determined by a combination of temperature-programmed desorption (TPD) and in situ DRIFTS. Activity and selectivity were measured in steady-state reaction and in temperature-programmed surface reaction (TPSR). Shape-dependent differences are observed in surface adsorbates, their transformation temperatures, and the selectivity for dehydration, dehydrogenation, and decomposition. Ethoxide and acetate are the primary surface species present under both TPD and TPSR conditions for all shapes. Different rates of α- and β-CH bond scission on the different shapes are responsible for different product selectivity. Structure-dependent, reductive vacancy formation and availability of reactant O_2 combine to control surface H which in turn plays a role in controlling product selectivity.

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1. Introduction

Ceria (CeO_2) possesses many attractive properties that make it a highly promising material for diverse applications such as solid electrolytes or anode materials in solid oxide fuel cells, automotive catalysts, and oxygen sensors, and there are books and reviews describing synthesis and catalytic applications [1–3]. Reducibility and oxygen storage capacity of pure CeO_2 and of CeO_2 doped with components such as Zr or other rare earths has long been of interest in emission control catalysis because of the ability of the CeO_2 to store and supply oxygen during variable ratios of fuel/oxygen [3–5]. CeO_2 has also found application as a support for various catalytic reactions including water–gas shift [6] and for partial oxidation, autothermal, or steam reforming of methanol or methane [7,8].

Many methods have been reported for the synthesis of CeO_2 including as ultra-small particles [9], as mesoporous structure morphologies [10,11], and with controlled shapes including cubes, octahedra, and rods [12,13]. In the latter case, the shapes of these particles result from termination on different specific crystallographic planes; {1 0 0} for cubes, {1 1 1} for octahedra and a mixture facets for rods [14,15], although recent results indicate that

depending upon synthesis and calcination conditions, rods may facet primarily to {1 1 1} [16,17]. These faceted nanoparticles offer the opportunity to probe the effect of surface structure (crystallographic termination) upon the activity, reducibility, and pathway selectivity. CeO_2 nanocrystals exhibit a shape-dependent behavior in some catalytic processes. For example, rods and cubes exhibit a greater capacity to store oxygen than polyhedra terminated primarily in {1 1 1} facets [12], and the rate of oxidation of CO catalyzed by CeO_2 nanorods is greater than by traditionally grown CeO_2 nanoparticles with undifferentiated shapes [15]. DFT calculations have demonstrated that the surface energies of these surfaces in vacuum follow the order (1 1 1) < (1 1 0) < (1 0 0) [18,19]. Vacancy formation energy, an important parameter for reducibility, is predicted to be largest for the (1 1 1) and smallest for the (1 1 0). Previous CO TPD [20] and H_2 TPD [21] have shown that cubes are easier to reduce than octahedra. Reduction of rods may be affected by defects and the facets present which depends upon preparation methods [16,17]. We have previously demonstrated that intrinsic Frenkel defects are present in greatest abundance on rods and least on the octahedra [22]. In addition, reduction-induced defects, probed by O_2 adsorption, are more difficult to induce on octahedra than on cubes and rods, a trend that follows the predicted vacancy formation energy. We have concluded these differences in surface oxygen vacancy formation energy, along with the nature and amount of low coordination sites and defect sites, are
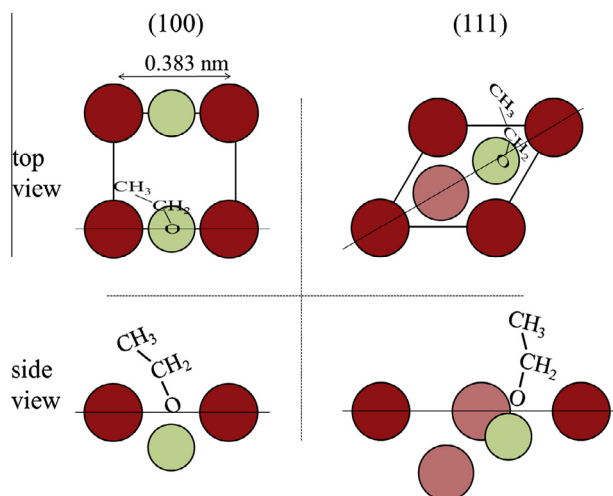
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ultimately the driving forces that control the CO oxidation performance [20].

It is of interest to understand the role of surface structure in controlling activity and selectivity in catalytic reactions involving the conversion of oxygenates. Selective oxidation of ethanol is a reaction in which it is important to balance reactivity with selectivity in order to achieve either the desired carbon-containing products or to control the H_2 to H_2O product ratio for applications using ethanol as a H_2 carrier. Dehydration vs. dehydrogenation selectivity in the conversion of alcohols catalyzed by oxides provides a model reaction where bifunctional pathways may be of critical importance in controlling selectivity [23]. In such pathways the proximity or coordination of acid and base sites on an oxide surface can lead to cooperativity and therefore dependence upon the geometry of surface sites. Acid–base cooperativity has been suggested to explain selectivity differences in conversion of alcohols to α-olefin [24] and in cis–trans selectivity in olefin products [25]. CeO_2 has versatile acid–base properties [26] and is an amphoteric oxide having both acid sites for stabilizing an anionic adsorbate and also base oxide sites for proton abstraction. The site geometry for (100) and (111) faces of CeO_2 vary as shown in Scheme 1. Through the use of the CeO_2 nanoshapes, the effect of coordination geometry of the acidic Ce cation sites and the basic O anion sites can be tested.

Among oxide catalysts, CeO_2 and CeO_2-based materials have been intensively studied as supports for Au [27], Pd [28], Pt [29], or other metals [30] for partial oxidation of ethanol primarily to extract its H_2 [31]. These technologies generally take advantage of the excellent redox property and high oxygen storage capacity (OSC) of ceria and doped ceria. Oxygen availability, which we now know is affected by the surface structure of the CeO_2, may be expected to affect the selectivity in such reactions. Shaped CeO_2 nanoparticles, rods and cubes, have been used a supports for Au in studies of water–gas shift reactions [32] and for steam reforming of methanol [33]. But there has been less work to explore the selectivity of reactions of oxygenates on metal-free oxides, especially for oxides with controlled shapes.

Therefore, we have studied the selective oxidation of the ethanol reaction over CeO_2 nanoshapes to investigate how surface structure affects the surface chemistry and selectivity. As a first step, we have compared ethanol adsorption, temperature-programmed desorption, temperature-programmed reaction, steady-state reaction selectivity, and used *operando* DRIFTS to determine the surface species present under reaction conditions. We find that the different CeO_2 shapes behave quite differently with respect to catalytic activity, selectivity and in their reaction pathways, and these differences are attributed to differences in the surface structure of the CeO_2. These results provide a first step to detailed theoretical understanding of the structure-reactivity relationships in this model catalytic reaction.

2. Experimental

2.1. Synthesis and characterization of the CeO_2 nanoshapes

Single-crystalline CeO_2 octahedra, rods, and cubes were prepared by hydrothermal processes, as we have used previously [22], following published methods [12,13]. After the hydrothermal synthesis, the white precipitates were collected and dried at 60 °C for several hours to obtain the "as-synthesized" material. These materials were characterized by X-ray diffraction (XRD) and electron microscopy as described previously [22]. Additional micrographs are provided in the Supplemental Information (Fig. S1). XRD data of all ceria samples could be indexed to the pure fluorite cubic structures. Transmission electron microscopy was routinely run for each synthesized batch to assure the desired shapes were reproducibly obtained. Typically, the rods are about 10 nm across and 50–200 nm long. According to previous studies [12,14,15], the synthesized rods grow along the [110] direction and are thought to expose {110} and {100} surfaces. The cubes range in size from 20 to 100 nm, but all in perfect cubic shape, exposing the {100} surface. The octahedra are very uniform in size distribution and shaped as almost perfect octahedra with little truncation, so they are dominated by {111} surface termination. The shapes of the three ceria polymorphs are preserved under calcination at temperatures below 500 °C. Both rods and cubes start to initiate morphology changes at 500 °C, but octahedra are thermally stable to 600 °C [22]. Surface areas of the as-synthesized samples were measured via nitrogen adsorption at 77 K using a Micromeritic Gemini 275 system. The Brunauer–Emmett–Teller (BET) areas of the rods, cubes, and octahedra are 80, 27, and 13 m^2/g, respectively.

2.2. Transient FTIR experiments

FTIR spectroscopy was conducted in a diffuse reflectance cell (HC-900, Pike Technologies, cell volume about 6 cm^3) in a Nicolet Nexus 670 FTIR spectrometer using a MCT/A detector with a spectral resolution of 4 cm^{-1}. After the desired pretreatments, a background spectrum was collected from the sample using 256 scans and 4 cm^{-1} resolution. Diffuse reflectance FTIR spectra (DRIFTS) were obtained by subtracting the background spectrum from subsequent spectra and are reported herein. Gases leaving the DRIFTS cell were analyzed using a downstream gas sampling quadrupole mass spectrometer (QMS, Pfeiffer–Balzer Omnistar) equipped with a 1-m-long gas-sampling capillary followed by an entrance aperture into the turbo-pumped QMS chamber.

Prior to data collection, the as-synthesized CeO_2 was pretreated at 450 °C for 1 h in a flowing gas stream of 2%O_2/He and then cooled to room temperature in He. Then, a selected gas stream was introduced onto the sample. The gas stream was either ethanol in He (25 mL/min He bubbling through a ethanol saturator at 0 °C calculated to yield 1.6% ethanol) or a reaction mixture of 2%O_2/He (9.5 mL/min) plus ethanol/He (25 mL/min) yielding a 2.1:1 ratio of ethanol/O_2. The temperature was then raised (ramping rate at

Scheme 1. Site geometry of the (100) and (111) surfaces with adsorbed ethoxide are shown schematically in top view and a side view. Lattice oxygen (red balls), Ce cations (green balls). Only first and second layers of a single surface cell are shown for clarity. Cartoon structures are based upon the ideal termination of a (111) surface and the (100) surface reconstructed as proposed to remove charge imbalance [61]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)