On the structure dependence of CO oxidation over CeO$_2$ nanocrystals with well-defined surface planes

Zili Wu [a,b,*], Meijun Li [a], Steven H. Overbury [a,b,*]

[a] Chemical Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States
[b] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States

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ABSTRACT

CO oxidation is a model reaction for probing the redox property of ceria-based catalysts. In this study, CO oxidation was investigated over ceria nanocrystals with defined surface planes (nanoshapes) including rods ({110} + {100}), cubes ({100}), and octahedra ({111}). To understand the strong dependence of CO oxidation observed on these different ceria nanoshapes, in situ techniques including infrared and Raman spectroscopy coupled with online mass spectrometer, and temperature-programmed reduction (TPR) were employed to reveal how CO interacts with the different ceria surfaces, while the mobility of ceria lattice oxygen was investigated via oxygen isotopic exchange experiment. CO adsorption at room temperature leads to strongly bonded carbonate species on the more reactive surfaces of rods and cubes but weakly bonded ones on the rather inert octahedra surface. CO-TPR, proceeding via several channels including CO removal of lattice oxygen, surface water–gas shift reaction, and CO disproportion reaction, reveals that the reducibility of these ceria nanoshapes is in line with their CO oxidation activity, i.e., rods > cubes > octahedra. The mobility of lattice oxygen also shows similar dependence. It is suggested that surface oxygen vacancy formation energy, defect sites, and coordinatively unsaturated sites on ceria play a direct role in facilitating both CO interaction with ceria surface and the reactivity and mobility of lattice oxygen. The oxygen vacancy formation energy, nature and amount of the defect and low coordination sites are intrinsically affected by the surface planes of the ceria nanoshapes. Several reaction pathways for CO oxidation over the ceria nanoshapes are proposed, and certain types of carbonates, especially those associated with reduced ceria surface, are considered among the reaction intermediates to form CO$_2$, while the majority of carbonate species observed under CO oxidation condition are believed to be spectators.

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1. Introduction

Cerium oxide and ceria-containing materials have received intense investigation as catalysts and catalyst supports for use in variety of catalytic reactions [1–9]. These applications generally take advantage of the excellent redox property and high oxygen storage capacity (OSC) of ceria. Therefore, great effort has been devoted to understanding the special redox property of ceria and to exploring ways to improve this property [10–18]. CO oxidation, a primary function of three-way catalytic convertors containing ceria catalysts, is a prototype model reaction for probing the redox property of ceria catalysts. CO oxidation is believed to proceed via Mars–van Krevelen mechanism over ceria [1,19], namely, it involves the removal of surface lattice oxygen by CO and consequent annihilation of vacancies by gas phase oxygen. The removal of surface oxygen, i.e., oxygen vacancy formation, is the rate determination step

(RDS) since the reoxidation with O$_2$ is very facile for reduced ceria. Extensive experimental and theoretical studies have been devoted to understanding CO oxidation over ceria catalysts [11,15,17,20–28]. A general consensus has been reached that CO interaction with ceria is structure dependent. Previous studies on polycrystalline ceria with differently exposed crystal planes already implied that CO oxidation is structure sensitive on ceria [17]. Recently, thanks to the advance of nanomaterial synthesis, ceria nanocrystals with controlled crystallographic planes [11,15,16,28–32] such as ceria rods and cubes, exposing crystal planes of {110} + {100} and {100}, respectively, have been successfully obtained and compared with multifaceted ceria nanoparticles for CO oxidation. It has been shown that ceria nanocrystals exposing reactive {110} and {100} planes on the surface are more active for CO oxidation than those dominated by {111} surfaces. The structure dependence of CO oxidation activity is explained largely based on theoretical work [33,34], which suggests that the oxygen vacancy formation energy is surface sensitive, following the sequence {110} < {100} < {111}. In order to understand the CO oxidation mechanism over different ceria surfaces, a number of theoretical studies have been dedicated to the

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interaction between CO and ceria surfaces [22,23,25–27,35–37]. The calculations show structure selectivity for CO adsorption, predicting weak CO adsorption for the most stable {1 1 1} surface and stronger chemisorption on more open surfaces, such as the {1 1 0} and {1 0 0}. The strong binding of CO to these ceria surfaces is mediated by the formation of carbonate-like complexes [23]. These investigations point to the direction of improving the redox property of ceria catalysts *via* utilizing ceria nanocrystals with more open surface structures.

Despite the intensive experimental and theoretical studies of CO adsorption and oxidation on ceria catalysts, there is still a lack of spectroscopic investigation of how CO interacts with different ceria surfaces and what the reaction mechanism is. Also lacking is the understanding of how the surface and bulk oxygen reactivity and mobility are affected by the surface structure of ceria, which could also have an impact on CO oxidation behavior. In this work, along the lines of our recent work [10] using ceria nanocrystals with define surface structures (nanoshapes), *in situ* vibrational spectroscopy including infrared and Raman will be employed to study the nature of the interaction of CO with three distinct ceria nanoshapes: rods ({1 1 0} + {1 0 0}), cubes ({1 0 0}), octahedra ({1 1 1}). We provide molecular-level insights into the surface dependence of CO oxidation over ceria catalyst and the mechanism of CO oxidation. Our results show that CO adsorption and reaction with ceria, and the reactivity and mobility of lattice oxygen are strongly influenced by the surface structure of ceria, thus leading to the nanoshape dependence of CO oxidation. The majority of carbonate species observed under steady state CO oxidation are reaction spectators while carbonate species associated with reduced Ce cations are possibly among the reaction intermediates in CO oxidation over ceria catalysts.

2. Experimental

2.1. Material synthesis

The synthesis of the three ceria nanoshapes has been described in detail in our recent paper [10]. Briefly, CeO_2 octahedra, rods, and cubes were prepared by hydrothermal process [16,29] in Teflon-lined stainless steel autoclaves at different hydrothermal temperatures and durations. For CeO_2 octahedra, 0.434 g $Ce(NO_3)_3 \cdot 6H_2O$ (ARCOS, 99.50%) and 0.0038 g $Na_3PO_4 \cdot 12H_2O$ (EM Science) precursors were used. 0.868 g of $Ce(NO_3)_3 \cdot 6H_2O$ and 9.6 g NaOH (BDH) were used as precursors to obtain ceria rods and cubes. After the hydrothermal treatment, fresh white precipitates were separated by centrifugation, washed with deionized water and ethanol several times, followed by drying at 333 K in air overnight. Nitrate species were detected on ceria rods and cubes while phosphate species on octahedra by Raman spectroscopy [10]. The amount of P on the ceria octahedra surface was determined by XPS to be small (P/Ce atomic ratio around 0.16). Although P has been found detrimental to the redox property of ceria catalyst, previous study indicated that the effect is relatively limited at XPS P/Ce ratio <0.2 (corresponding to bulk P/Ce < 0.03) [38]. So it is still reasonable to attribute our experimental observations largely to the surface structure effect of octahedra rather than P poisoning.

2.2. Material characterizations

XRD patterns of the ceria nanocrystals were collected on a PANalytical powder diffractometer using Cu Kα radiation. The electron microscopy images of the ceria nanocrystals were recorded on a Zeiss Libra 120 TEM and Zeiss Merlin VP SEM/STEM systems. Brunauer–Emmett–Teller (BET) surface area of the 623 K calcined

ceria nanocrystals was measured *via* nitrogen adsorption at 77 K by using a Micromeritic Gemini 275 system.

2.3. CO oxidation performance

CO oxidation over the ceria nanoshapes was tested on a plug-flow, temperature-controlled microreactor system (Altamira AMI 200). The sample (ca. 50 mg) was well-mixed and diluted with quartz sand to a similar volume to minimize diffusion limitations. The sample, loaded into a U-shaped quartz tube (4 mm i.d.) and supported by quartz wool, was pretreated in flowing 5% O_2/He (30 mL/min) at 673 K for 1 h and cooled down to room temperature (rt) in O_2/He atmosphere. The gas was switched to the reaction mixture (30 mL/min 5% O_2/He + 10 mL/min 2% CO/2%Ar/He; O_2: CO = 7.5) at rt, and the system was ramped up to 673 K and cooled back to rt at a rate of 1 K/min. A portion of the product gas stream was extracted periodically with an automatic sampling valve and analyzed using a dual-column gas chromatograph with a thermal conductivity detector. All gases, unless specified, were provided by Air Liquide with the UHP helium as balance gas, with moisture content less than 1 ppm.

2.4. Temperature-programmed reduction and desorption (TPR and TPD) and oxygen isotopic exchange

CO-TPR, TPD, and oxygen isotopic exchange over ceria samples (ca. 30 mg) were also conducted on the AMI microreactor system. Before each of the experiments, the ceria sample was pretreated in flowing 5% O_2/He (30 mL/min) at 673 K for 1 h and cooled down to rt and switched to helium purging for 30 min.

- For TPD, the pretreated sample was exposed to 2% CO/2%Ar/He (30 mL/min) at rt for 30 min and then purged with helium at rt for 45 min. Then the sample was heated (10 K/min) up to 690 K in flowing helium and hold for another 30 min.
- For CO-TPR, the pretreated sample was exposed to 2% CO/2%Ar/He (30 mL/min) at rt for 30 min and then ramped (10 K/min) up to 1073 K and held for another 30 min. In both CO-TPR and CO-TPD, the gas stream was analyzed by an online quadrupole mass spectrometer (QMS) (OmniStar GSD-301 O2, Pfeiffer Vacuum).
- For oxygen isotopic exchange, the pretreated sample was exposed to 1% $^{18}O_2$/He (30 mL/min) at rt and ramped (10 K/min) up to 1100 K. The oxygen isotopomers (32, 34, and 36) were monitored by the online QMS.

2.5. In situ spectroscopy

IR spectra were collected using a Thermo Nicolet Nexus 670 spectrometer in diffuse reflectance mode (DRIFTS) while the exiting stream was analyzed by QMS [39,40]. A Pike Technologies HC-900 DRIFTS cell with nominal cell volume of 6 cm³ was used. Before each of the following IR experiments, the ceria sample was pretreated in the DRIFTS cell in flowing 2% O_2/He (25 mL/min) at 693 K for 1 h and then cooled to rt before switching to He.

- In CO adsorption experiments, the pretreated sample was purged with helium at rt before switching to 2%CO/2%Ar/He (25 mL/min) flow for 30 min.
- In temperature-programmed reduction experiments (CO-TPR-IR), the pretreated ceria sample was exposed to flowing 2%CO/2%Ar/He (25 mL/min) for 30 min at rt and then ramped (10 K/min) up to 773 K in the same gas.
- In CO oxidation experiments, the ceria sample was pretreated at 693 K, purged in He at 693 K and then exposed to the reaction mixture (20 mL/min 2% O_2/He and 5 mL/min 2%CO/2%Ar/He;