

## CO and CO<sub>2</sub> interaction on CeO<sub>2</sub> nanocube and nanorod surfaces studied by DRIFTS

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### Resumo/Abstract

RESUMO – As análises espectroscopia de infravermelho por transformada de Fourier de reflectância difusa (DRIFTS) com CO/CO<sub>2</sub> foram usadas para investigar o efeito da forma da céria (cubos versus bastões) nas interações químicas da superfície. Os resultados iniciais sugerem que a morfologia influencia o modo de adsorção, indicando que os bastões podem oferecer maior versatilidade para síntese de álcool superiores a partir da conversão de CO/CO<sub>2</sub>.

*Palavras-chave: Morfologia do CeO<sub>2</sub>, DRIFTS, interação na superfície, CO/CO<sub>2</sub>, álcoois superiores.*

ABSTRACT – CO/CO<sub>2</sub>-diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analyses were conducted to investigate the effect of ceria shape (cubes versus rods) on surface chemical interactions. Initial results suggest that morphology influences adsorption mode, indicating that rods could offer greater versatility for higher alcohol synthesis from CO/CO<sub>2</sub> conversion.

*Keywords: CeO<sub>2</sub> morphology, DRIFTS, surface interaction, CO/CO<sub>2</sub>, higher alcohols.*

### Introduction

Cerium oxide (CeO<sub>2</sub>) is commonly used as a support due to its unique features: versatile acid-base catalytic chemistry and excellent redox capacity (Ce<sup>4+</sup>/Ce<sup>3+</sup> pair), in which oxygen vacancies (O<sub>vac</sub>) can easily be generated on the surface [1]. Distinct ceria morphologies can be synthesized with specific physical-chemical properties. The shape-dependence, mainly the facet dispositions and O<sub>vac</sub> content, would affect the performance of CeO<sub>2</sub>-based catalysts [1]. Herein, ceria nanocubes and nanorods were initially synthesized and characterized to investigate the influence of morphology on probe-molecule interactions on the CeO<sub>2</sub> surface. A preliminary CO and CO<sub>2</sub>-DRIFTS study was used to monitor the ceria surface, focusing on relevant information that could guide the design of efficient CeO<sub>2</sub>-based catalysts for higher alcohol synthesis (HAs).

### Experimental

#### *Synthesis of CeO<sub>2</sub> nanoparticles*

The CeO<sub>2</sub> nanorods (CeO<sub>2</sub>-NR) and nanocubes (CeO<sub>2</sub>-NC) were synthesized according to Tana et al.'s protocol [1]. The hydrothermal syntheses were conducted at 100 °C for CeO<sub>2</sub>-NR and 180 °C for CeO<sub>2</sub>-NC during 14 h. The yellow (CeO<sub>2</sub>-NR) and beige (CeO<sub>2</sub>-NC) powders were obtained upon calcination at 400 °C for 4 h.

#### *Physical-chemical characterization*

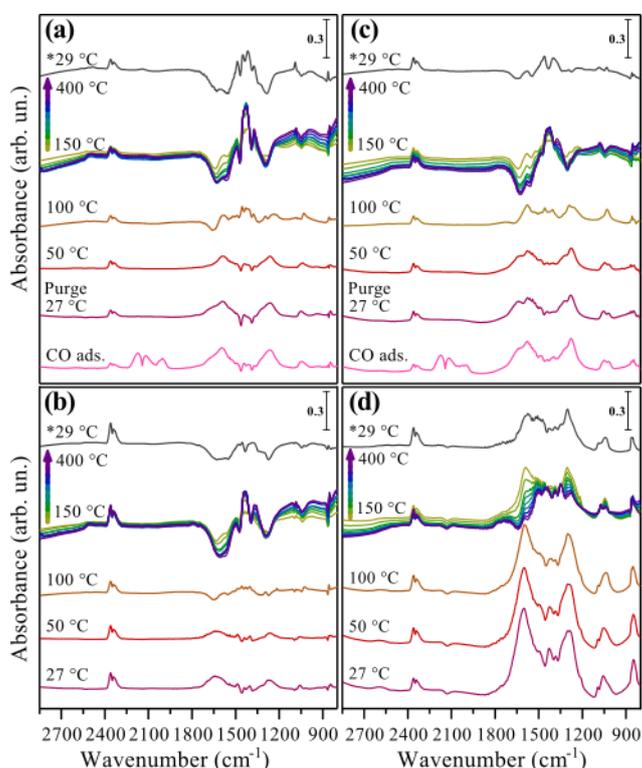
Powder X-ray diffraction patterns (XRD, 2θ = 20°-80° at 2° 2θ min<sup>-1</sup>) were recorded on a Bruker D8 diffractometer.

The crystallite sizes were calculated by the Debye-Scherrer equation - (111) peak. The Raman spectra were acquired by a LabRAM HR Horiba JobinYvon spectrometer (633 nm laser, 50% filter, 50-800 cm<sup>-1</sup>, resolution of 4.8 cm<sup>-1</sup>). N<sub>2</sub>-physisorption isotherms at -196 °C were performed on Micromeritics ASAP 2420. The specific surface area (S<sub>BET</sub>) was determined by the Brunauer-Emmett-Teller (BET) method. High-resolution transmission electron microscopy (HRTEM) images were acquired using a JEOL 2100F 200 kV MET-FEG instrument. *In situ* CO and CO<sub>2</sub>-DRIFTS spectra were collected using a Bruker Invenior R FTIR spectrometer (equipped with MCT detector and a Harrick cell). The samples were pre-treated at 400 °C for 2 h under pure H<sub>2</sub> flow (15 mL min<sup>-1</sup>). Afterward, the samples were cooled under He flow (15 mL min<sup>-1</sup>) to collect the background spectra (resolution of 4 cm<sup>-1</sup> and 256 scans per spectrum). The temperature was kept below 30 °C, then the materials were exposed to a CO flow (10% CO/He, 15 mL min<sup>-1</sup>) for 40 min or a CO<sub>2</sub> flow (15 mL min<sup>-1</sup>) for 25 min. Subsequently, the system was cleaned by purging He until the removal of the gas phase. The desorption process was monitored by heating up to 400 °C under He flow.

### Results and Discussion

HRTEM images confirm the formation of CeO<sub>2</sub> particles in cube and rod-like shapes. According to the SAED analysis, the identified crystalline phase corresponds to the fluorite-type cubic structure of CeO<sub>2</sub> (standard pattern, ICSD code 239412). XRD patterns corroborate with

HRTEM analysis, exhibiting the typical diffraction peaks for the CeO<sub>2</sub> phase [1]. The crystallite size values are 28.18 nm (CeO<sub>2</sub>-NC) and 8.63 nm (CeO<sub>2</sub>-NR), indicating a much larger crystallite size for cubes than rods, and consequently, a higher crystallinity degree and a lower structural defect density. In addition, the isotherms classification for both materials is type IV(a) with H3-type hysteresis loop [1]. The S<sub>BET</sub> values are 42 m<sup>2</sup> g<sup>-1</sup> (CeO<sub>2</sub>-NC) and 106 m<sup>2</sup> g<sup>-1</sup> (CeO<sub>2</sub>-NR). Moreover, the bands at 463 cm<sup>-1</sup> and 599 cm<sup>-1</sup> in Raman spectra are associated with the triply degenerate F<sub>2g</sub> active mode of fluorite-CeO<sub>2</sub> and lattice defects (O<sub>vac</sub>). The relative contents of O<sub>vac</sub> (peak area ratio, A<sub>599</sub>/A<sub>462</sub>) are 0.076 (CeO<sub>2</sub>-NR) > 0.049 (CeO<sub>2</sub>-NC). These values align with the crystallite size: a smaller size means a larger surface area and a higher A<sub>599</sub>/A<sub>462</sub> ratio (more O<sub>vac</sub> content).



**Figure 1.** *In situ* DRIFTS analysis on CeO<sub>2</sub>-NC (a,b) and -NR (c,d): CO (a,c) and CO<sub>2</sub> (b,d) adsorptions on reduced samples (\*cooling in He flow).

DRIFTS spectra are shown in Figure 1. In general, CO<sub>2</sub> and CO gas-phase are identified by a double band around 2350 cm<sup>-1</sup> and 2135 cm<sup>-1</sup>, respectively [2]. The overlapped contributions for carbon species adsorbed are observed in the region of 1800-800 cm<sup>-1</sup> [2]. Bidentate carbonates (bridge/chelate) bands are visualized at 1670-1578 cm<sup>-1</sup> (ν CO), 1280-1265 cm<sup>-1</sup> (ν<sub>asy</sub> COO), and 1018 cm<sup>-1</sup> (ν<sub>sy</sub> COO). The bands for ν<sub>asy</sub>(CO<sub>3</sub><sup>2-</sup>) at 1487-1463 cm<sup>-1</sup>, ν<sub>sy</sub>(CO<sub>3</sub><sup>2-</sup>) at 1320-1307 cm<sup>-1</sup> and ν(CO) at 1050 cm<sup>-1</sup> can be attributed to monodentate carbonate. Moreover, polycarbonates were identified at 1487-1463 cm<sup>-1</sup> and 1087-1050 cm<sup>-1</sup>. It can be

observed that distinct spectra profiles depend on the gas feed, temperature range, and CeO<sub>2</sub> surface morphology. The bands decrease when the temperature increases from 27 °C to 100 °C, indicating a consumption of these species (Fig. 1.a-d). However, the species' behavior on the ceria surface at 200 °C to 400 °C was changed. The consumption of bidentate species and the production of monodentate ones occurred. Besides that, a new signal emerges around 1430 cm<sup>-1</sup> when it reaches 400 °C. Its presence is linked to polycarbonate species, with signals at 1090 and 940 cm<sup>-1</sup>. The CeO<sub>2</sub>-NC spectra profiles slightly change within the temperature range, regardless of the probe molecules used (Fig. 1.a,b). Whereas CeO<sub>2</sub>-NR probed with CO exhibits low-intensity polycarbonate bands at 400 °C compared to other carbonate bands (Fig. 1.c). The spectrum profile at 1800-1200 cm<sup>-1</sup> was altered when CO<sub>2</sub> was adsorbed on CeO<sub>2</sub>-NR (Fig. 1.d). It is important to note that the molecule coordination mode depends on the dominant plane exposition ({110} - rods, and {100} - cubes) and their active sites [1]. The greater availability of {110} planes due to the larger S<sub>BET</sub> with high O<sub>vac</sub> content for CeO<sub>2</sub>-NR compared to CeO<sub>2</sub>-NC could favor its reactivity. From a mechanistic point of view, for HAs from the CO/CO<sub>2</sub> conversion [3], these carbonate species are key intermediates. Thus, a diversification of carbon species on the CeO<sub>2</sub>-NR surface, when changing the gas (CO or CO<sub>2</sub>), indicates that this morphology could be more versatile for CO/CO<sub>2</sub> conversion, driving the reaction pathway towards the HAs.

## Conclusions

A preliminary *in situ* CO and CO<sub>2</sub>-DRIFTS study was conducted to monitor the as-synthesized CeO<sub>2</sub> nanocubes and nanorods' surface. The CeO<sub>2</sub> morphology affected the CO/CO<sub>2</sub> adsorption mode, as revealed by the DRIFTS spectra profile of carbonate species formed. It could indicate a greater versatility of rods than cubes for HAs. Further analyses will be carried out under different conditions (e.g., pulse technique, saturation, or feed composition) to improve our understanding of the chemical surface. This will help us design efficient CeO<sub>2</sub>-based catalysts for the target reaction.

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