

Nanosized CeO₂ particles: Catalytic properties in CO oxidation.

Antonio Gómez-Cortés², Dora Solís^{1,2}, Jesús Arenas-Alatorre¹ and Gabriela Díaz^{1*}

¹Instituto de Física, Universidad Nacional Autónoma de México (UNAM), A. P. 20-364 México D. F. 01000 México. ²Facultad de Química, UAEM, Toluca, Estado de México, México. diaz@fisica.unam.mx

Introduction

Cerium based materials have important applications in areas such as catalysis, high-temperature ceramics and fuel cells [1-2], among others. The technological importance of ceria is linked to the Ce⁴⁺/Ce³⁺ redox couple which allows the material to act as an oxygen buffer by storing and releasing oxygen. The redox and catalytic properties of CeO₂ and related materials are linked to the crystal size and to structural defects as oxygen vacancies. In particular, it has been reported [3] that for CeO₂ nanocrystals < 10 nm a noticeable increase in the redox properties is observed. In general a decrease in the size of the crystal leads to an augmentation of the surface area and to a change in morphology which provide the appearance of potentially active sites. Theoretical studies have shown that the stability of low index planes follows the order (111) (110) (211) (100) while their reactivity follows the opposite [4]. Preservation of high surface area after calcination at high temperature would be a key step to obtain ceria with enhanced redox properties.

Materials and Methods

CeO₂ powder samples were prepared by two methods: homogeneous precipitation using urea and a surfactant-assisted approach (Brij35 and Hexadecylamine as surfactants). Cerium nitrate (Ce(NO₃)₃) was used as inorganic precursor. Materials prepared using surfactants were calcined at 300 and 500 °C, while CeO₂ obtained by precipitation was calcined in the range 300-800 °C. Samples are identified as BrijX, HAX and PUX where X is the calcination temperature. Samples were characterized using TGA, N₂ adsorption, DRIFT, TPR, XRD and HRTEM (JEM2010F). The oxidation of CO in the range 150-500°C was carried out in a fixed-bed reactor system (RIG-100) at high GHSV values to minimize the effect of mass and heat transfer phenomena. Prior to catalytic run all catalyst samples were pretreated in-situ in air flow at 300 °C for 1 h and cooled to room temperature in He. Product and reactant analysis was carried out by gas chromatography (TCD) with a Carboxen 1000 packed column.

Results and Discussion

CeO₂ prepared by surfactant-assisted route presented high surface area after calcination at 500 °C (167-192 m²/g) with a crystal size below 10 nm. Samples prepared by precipitation presented lower surface areas with a crystal size around 54 nm when calcined at 800 °C. DRIFT spectroscopy confirmed the elimination of the template in Brij samples after calcination at 300 °C. On the other hand, strongly adsorbed carbonate species were detected in these samples. XRD patterns showed the fluorite type structure of ceria and refinement of the crystal structure by Rietveld showed an increase in the cell parameter of the CeO₂ as the crystal size decreases (Table 1). This behavior indicates the likely presence of Ce³⁺ in the samples. Light off curves of CO oxidation (% of CO transformed vs. T) showed the typical behavior as a function of the calcination temperature being the PU800 CeO₂ the less active catalyst. Specific activity measured at 325 °C is shown in Table 1. As a general trend, specific activity

decreases as the crystal size increases regardless the preparation method. However, it is interesting to note that preparation method leads to slightly different reactive CeO₂ surfaces as observed from the activity values. In the PU series activity drops by a factor 2 as the crystal size increases 5 times (PU300 and PU800 samples). HRTEM morphological characterization showed the presence of (100) planes in the PU300 ceria while mostly (111) planes were present in the PU800 sample. Brij300 and HA300 powders exposed as in the PU300 sample (100) planes. Aneggi et al. [5] have shown the role of reactive surfaces of the {100} type in CO oxidation over polycrystalline ceria powders. Characterization of the redox properties of the samples as well as characterization of oxygen vacancies by Raman spectroscopy is in progress.

Significance

Contribution to the understanding of structure-reactivity relations in ceria based catalysts.

Table 1. Textural and catalytic properties of ceria powders.

Sample	S _{BET} (m ² /g)	Lattice parameter a (nm)	Crystal Size (nm)	Specific rate at 300°C (mol/m ² h)×10 ⁴
Brij300	239	0.54147(4)	6.1(5)	7.3
Brij500	167	0.54128(3)	8.3(6)	6.2
HA300	161	0.54152(2)	7.5(5)	5.6
HA500	192	0.54150(2)	9.7(7)	4.1
PU300	123	0.54259(2)	11.2(1)	9.7
PU500	78	0.54165(2)	12.9(1)	8.4
PU800	10	0.54123(1)	53.6(4)	4.5

Acknowledgements

Acknowledging L. Rendón of LCMIF, M. Aguilar and CONACYT for HRTEM images, DRX spectra and funding through the project 42666F, respectively.

References

1. Trovarelli (Ed), Catalysis by ceria and related materials, Catalytic Science Series, Vol. 2, Imperial College Press 2002.
2. Rocchini, A. Trovarelli, J. Llorca, G.W. Graham, W.H. Weber, M. Maciejewski, and A. Baiker, *J. Catal.* 194,461 (2000).
3. Spainier E., Robinson R.D., Zhang F., Chan S., Herman I.P., *Phys. Rev. B* 64,245407 (2001).
4. Conesa C.J., *Surf. Sci.*,339, 337 (1995).
5. Aneggi E.,Llorca J., Boaro M., Trovarelli A., *J. Catal.* 234, 88(2005).