Novel aerosol-made CuO-CeO_2 catalysts with superior CO oxidation activity

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Introduction

Among the alternatives to the noble metal-based systems for the abatement of carbon monoxide, Cu is often chosen to enhance the ceria reactivity, and the system has proven to be promising [1,2]. Moreover, beneficial effects on catalytic performance have been evidenced when favoring (i) a stronger interaction between CuO and CeO_2, (ii) higher specific surface area, (iii) small pores with a homogeneous distribution [3]. Nevertheless, in this system, most catalysts reported in literature are synthesized by methods that neither allow to precisely control textural and morphological properties nor favor an intimate mixing between the two phases. Exploring innovative catalysts syntheses is arguably the keystone to round these corners and to reach higher catalytic performance. Along this line, the aerosol-assisted sol-gel process (AASG), which is emerging as a powerful route to produce various nanomaterials and in particular tailored heterogeneous catalysts [4,5] is primed to solve the above-mentioned challenges. Here we report, for the first time, aerosol-assisted sol-gel made CuO-CeO_2 catalysts employed for the Low Temperature CO Oxidation (LTCO).

Materials and Methods

AASG catalysts have been synthesized by atomization of a precursors solution (cerium and copper nitrates with a templating agent, in an ethanol/water solution), followed by rapid processing (reactive drying) in a tubular furnace. Templating agent removal and porosity formation has been carried out by a controlled calcination step under static air, up to 723 K. Aerosol made materials (denoted as A-CuxCe, where "x" is the Cu wt.% loading) are then compared with a series of catalysts made by dry impregnation of copper over AASG-synthesized pristine ceria (denoted as I-CuxCe). Catalysts were tested for both CO oxidation and ethylene oxidation (using a mixture containing 1000 ppm of CO or 500 ppm of ethylene + 10% O_2 in N_2) using a temperature ramp or sets of isothermal steps, with an online IR monitoring of reactants/products concentrations. Performance is interpreted in the light of in-depth characterization surveys (XRD, in situ XRD, N_2 physisorption, DR-UV-Vis, TPD, XPS, Raman, (S)TEM, EDX).

Results and Discussion

Structural and textural characterization revealed that CeO_2 made by AASG technique is a promising support with suitable properties for LCTO reaction. For example, XRD patterns show that the while commercial CeO_2 is composed of 40 nm-sized crystallites aerosol derived CeO_2 features much smaller crystallites (8 nm). Aerosol-made CeO_2 had a specific surface area (SSA) as high as 130 m^2/g, with a narrow pores distribution centered around 5-6 nm, while the commercial ceria shows only a SSA of 5 m^2/g and a bigger pore distribution centered at 25 nm. The aerosol-made ceria is composed of small CeO_2 crystallites (x nm, via Scherrer) featuring a high abundance of oxygen vacancies (via Raman). Upon introduction of Cu , textural and structural features are maintained. STEM micrographs show (Fig. 1, A-C) that Cu thoroughly dispersed throughout the ceria microspheres when using the one-port procedure. When using the dry impregnation technique, the ceria microspheres are destroyed, and Cu nanoparticles, with diameter ≤ 3 nm, are homogeneously dispersed on 10-15 nm CeO_2 nanoparticles (Fig. 1, D-F). Such materials with a high surface area and porosity and small and dispersed crystallites showed superior catalytic activity, markedly outperforming a series of state-of-the-art benchmark catalysts (i.e., Pd-Al_2O_3, Cu impregnated over commercial CeO_2 nanopowders, Cu-CeO_2 catalysts prepared in a vortex reactor [2], commercial three-way catalyst Pd-Rh/CeO_2-ZrO_2 (TWC)). Aerosol-made catalysts achieve $T_{90\%}$ conversion at 80-82 °C (Fig. 1, G). We will also show and discuss the fact that superior catalytic activity is maintained even oxygen-poor atmosphere, and that the new catalysts also perform outstandingly in ethylene total oxidation.

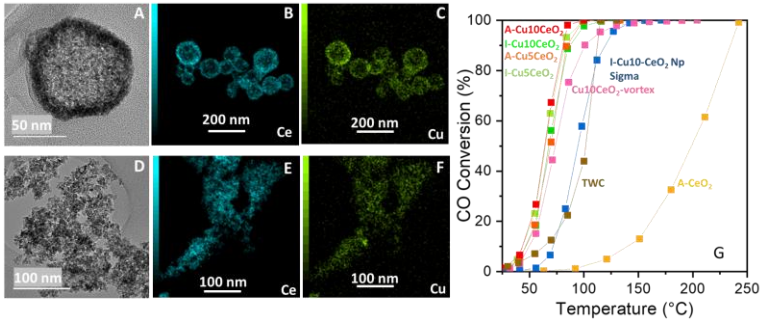

Figure 1.: HRTEM/STEM analyses and elemental mapping for (A,B,C) A-Cu10CeO_2 catalyst and (D, E, F) I-Cu10CeO_2 catalyst. (G) CO oxidation light off curve obtained with the catalysts developed in this study and with an industrial reference (three way catalyst, TWC)s.

Significance

This work proves that it is possible to circumvent the use of depleting noble metals for the production highly efficient low-temperature total oxidation catalysts. The key is the aerosol method, which is a direct, rapid, continuous, and scalable way to prepare tailored porous materials with the desired textural/structural properties and excellent dispersion of the Cu NP. In particular, for the scale up of the manufacturing process, simply feeding the atomizer for longer timespans allows accumulating, continuously, large quantities of the same desired materials and even at the lab scale it is possible to obtain from 10 to 50 g of catalysts in less than an hour.

References

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