Morphological influence of nanostructured supports in CuO-CeO₂ (rods, cubes and spheres) catalysts on the WGS activity and stability.

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Introduction

The water-gas shift reaction (WGS, CO + H₂ → CO₂ + H₂), is one of the essential steps for hydrogen production/purification [1]. The WGS processes can be found in industry as the high-temperature (HT-WGS) and low-temperature shift (LT-WGS) processes which employ Fe-Cr catalysts and Cu/ZnO/Al₂O₃ catalysts, respectively. CuO-CeO₂ catalysts have been proposed as a new variant for the low temperature process, showing great promise by synergistic interaction between Cu and Ce. Typically, for ceria supports, three morphologies are most commonly synthesized and studied, including nanorods, nanocubes and nanospheres. Among the three, ceria nanorods, which mostly expose (100) and (110) faces, were reported as the best catalyst support for a range of reactions including: CO oxidation, NO reduction, CO₂ reforming of methane, and preferential CO oxidation. The reasons for the ceria nanorod being a superior catalyst support were commonly attributed to the high mobility of oxygen over the (110) faces as well as a strong metal-support interaction that tends to stabilize and anchor the metal centers. CuO/CeO₂ is one of the most widely studied nonprecious metal ceria catalysts for the low-temperature WGS. A strong synergistic interaction between Cu and ceria affects the WGS activity of the catalyst, but details of this interaction on different ceria crystal faces and how the different crystal faces affect the performance of the catalysts remain unclear. In this work, we examined three CuO/CeO₂ catalysts with different nanostructured ceria supports using operando XRD, XAFS, DRIFTS and high resolution electron microscopy (HR-TEM, STEM) to probe the relationship between the ceria morphology, the interaction between cerium oxide and copper, and the catalytic pathways of the WGS.

Materials and Methods

The ceria nanospheres (ns), nanorods (nr) and nanocubes (nc) were synthesized (Fig 1) according to wet chemical methods previously reported in the literature [2]. Copper was incorporated by incipient wetness impregnation using copper nitrate as precursor (5 wt.% Cu loading). The samples were dried overnight at 100 °C and calcined in air at 500 °C for 2 h. X-ray diffraction measurement of the WGS reaction were performed at the X7B beamline (λ=0.3196 Å) of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) using an in-situ gas flow cell with a resistance heater. Time-resolved in operando XAFS measurements were performed at the X19A beamline of the NSLS, with the same in-situ cell, gas flow conditions and temperature programs used in the XRD measurements. The HR-TEM and STEM images were collected at the CFN (BNL) using a JEOL JEM 2100F instrument operating with an accelerating voltage of 200 kV and an aberration-corrected Hitachi HD-2700C, a dedicated scanning transmission electron microscope, operated at 200 kV. In-situ DRIFTS using a Bruker Equinox 55 FTIR spectrometer equipped with a modified Harrick Praying Mantis DRIFT flow cell. The composition of the outflow gas was analyzed by a MS-RGA instrument.

Results and Discussion

CuO/CeO₂ (ns) was the best WGS catalyst of the three studied in terms of both activity and stability. CuO/CeO₂ (nr) had slightly lower activity than CuO/CeO₂ (ns) and worse stability. CuO/CeO₂ (nc) had poor activity and only moderate stability (Fig 1). The concentration of defects and imperfections of the structured ceria support had a marked effect on the dispersed state of CuO and also on the particle size of the Cu metal during the WGS reaction. The presence of defects and imperfections in the oxide helped to give the CuO/CeO₂ (ns) catalyst the best activity and stability. The size of metallic copper particles formed under WGS reaction was strongly correlated to the WGS activity achieved in each case. This in turn could have an effect on the type of surface and/or surface defects present in each case and likely differences in surface area between the samples. DRIFTS indicated distinct surface chemistry prevailed on the three systems and that formates was not a key intermediate for the WGS reaction on the three CuO/CeO₂ catalysts. While specific carbonate species may act as poisons of active sites on the surface of the structured catalysts [3].

Significance

The nanostructured oxide supports offer the ability to influence the catalytic function especially on the nanometer scale of supports. Understanding the basic chemistry of these materials will lead to an ability to tailor new catalysts to better target reaction selectivity, activity, and stability.

Figure 1. Top –HR-TEM of nanospheres, nanorods and nanocubes of Cu- CeO₂. Lower left – Activity of catalysts in the WGS. Lower right – XRD of CeO₂ structure during WGS.

References

3. Y. Siyu et al., PCCP, 2014, 16(32), 17183-17195.

The work carried out at Brookhaven National Laboratory, the National Synchrotron Light Source and the Center for Functional Nanomaterials was supported by the US Department of Energy (Office of Basic Energy Science, Catalysis Science, DE-AC02-98CH10886).