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Structure sensitivity of the low-temperature water-gas shift reaction on Cu–CeO_2 catalysts

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ABSTRACT

We have investigated the structure sensitivity of the water-gas shift (WGS) reaction on Cu–CeO_2 catalysts prepared at the nanoscale by different techniques. On the surface of ceria, different CuO_x structures exist. We show here that only the strongly bound Cu–$[O_x]$–Ce species, probably associated with the surface oxygen vacancies of ceria, are active for catalyzing the low-temperature WGS reaction. Weakly bound CuO_x clusters and CuO nanoparticles are spectator species in the reaction. Isolated Cu^{2+} ions doping the ceria surface are not active themselves, but they are important in that they create oxygen vacancies and can be used as a reservoir of copper to replenish surface Cu removed by leaching or sintering. Accordingly, synthesis techniques such as coprecipitation that allow for extensive solubility of Cu in ceria should be preferred over impregnation, deposition–precipitation, ion exchange or another two-step method whereby the copper precursor is added to already made ceria nanocrystals. For the synthesis of different structures, we have used two methods: a homogeneous coprecipitation (CP), involving hexamethylenetetramine as the precipitating agent and the pH buffer; and a deposition–precipitation (DP) technique. In the latter case, the ceria supports were first synthesized at the nanoscale with different shapes (rods, cubes) to investigate any potential shape effect on the reaction. Cu–CeO_2 catalysts with different copper contents up to *ca.* 20 at.% were prepared. An indirect shape effect of CeO_2, manifested by the propensity to form oxygen vacancies and strongly bind copper in the active form, was established; i.e. the water-gas shift reaction is not structure-sensitive. The apparent activation energy of the reaction on all samples was similar, 50 ± 10 kJ/mol, in a product-free (2% CO–10% H_2O) gas mixture.

1. Introduction

The water-gas shift (WGS) reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) plays an important role in fuel processing. For PEM fuel cell applications, novel low-temperature WGS catalysts are under development to upgrade the hydrogen-rich reformate gas streams where the catalyst possesses improved activity and greatly improved stability over the commercial Cu–ZnO catalysts [1,2]. The latter have been optimized for the production of chemicals, and are not suitable for fuel cell applications as they are pyrophoric and deactivate fast after exposure to air and/or water condensation. Because of its high activity [3] and low price, copper is still an excellent candidate as the active component of a new generation, stable catalyst for the WGS reaction. Many promising such catalyst compositions use cerium oxide (ceria, CeO_2) carriers, with the latter actively contributing to the making of an active and stable Cu-based catalyst.

As one of the most important rare earth oxides, ceria has been extensively applied in catalysis, electrochemistry, and optics, due to its unique physical and chemical properties. CeO_2 retains its defective fluorite-type crystal structure during the oxygen storage and release processes, and thus is an active oxide component of various oxidation catalysts used in diverse redox catalytic reactions [4,5]. Ceria-based catalysts are very good WGS catalysts [6–10], and the Cu–CeO_2 system was first reported by Li et al. as a promising low-temperature shift catalyst [7]. The choice of Cu–CeO_2 for high-temperature WGS applications was also rationalized [10], because this copper-based system is more stable than the commercial Cu/ZnO. For a practical fuel cell system, operating under frequent shutdown and restart cycles, ceria needs to be modified by addition of zirconia [11,12] or another dopant to avoid formation of Ce(III) hydroxycarbonate during shutdown to RT in the water-containing reaction gas. Another approach is to regenerate the catalyst frequently by oxidation at 400–450 °C [11–13] or to run the reaction in oxygen-assisted mode [13]. Despite this issue,

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ceria and doped ceria remains the support of choice when a highly dispersed metal preparation is desired, which must remain stable over a wide temperature range [10]; and when surface oxygen availability to the metal is required, as in the case of the water-gas shift reaction [9].

During the last decade, copper–ceria catalysts have been widely studied for the WGS reaction *via* different approaches. Synthesis, structural and surface investigations by multiple characterization techniques, activity and stability tests, investigations of the reaction mechanism, and determination of the active sites have been addressed. For example, Wang et al. observed reversible redox properties of copper in $Ce_{1-x}Cu_xO_2$ by *in situ* XAFS and time-resolved XRD measurements [14], and further found a complex interaction between copper and the oxygen vacancies of ceria [15]. Koryabkina et al. found that the addition of ceria did not increase the WGS rate per unit of Cu surface area, and claimed that ceria is not a promoter for copper [16], while Djinović et al. reported that the activity of CuO–CeO_2 catalysts for WGS reaction was related to the extent of surface CeO_2 reduction and the interaction between CuO and CeO_2 [17]. Thus, the basic questions regarding the structure–activity relationship and the interaction of copper and ceria in the WGS reaction have been addressed, but often with divergent conclusions. In our opinion, a consensus must be reached soon to enable better catalyst designs and development of active and stable water-gas shift catalysts for practical fuel cell applications. This will potentially lead to novel, properly designed Cu-containing CeO_2 catalysts of comparable activity to the more expensive choices of Pt- or Au-based WGS catalysts.

In this work, we have used different preparation methods to obtain the copper–ceria materials, developed a structural model for each sample, and attempted to correlate the catalyst activity to the presence or absence of certain Cu species and their interaction with the surface of ceria. The latter is an important ligand to the formation and stabilization of the active copper sites.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of copper–ceria via coprecipitation (CP) method

$Ce(NO_3)_3{\cdot}6H_2O$ (99.5%, Alfa) and hexamethylenetetramine ($(CH_2)_6N_4$, > 99%, Alfa) were combined using a previously described procedure [18]. A solution of copper nitrate $Cu(NO_3)_2{\cdot}2.5H_2O$ (98.0–102.0%, Alfa), with a varying concentration to produce varying copper contents, was added to this reaction mixture under heating at 60–70 °C. The product was collected by filtration or centrifugation and then calcined in static air at 400 °C for 4 h.

2.1.2. Synthesis of copper–ceria via deposition–precipitation (DP) method

Rod- and cube-shaped CeO_2 supports were prepared *via* a controlled hydrolysis procedure, followed by a hydrothermal treatment [19]. The as calcined (air, 400 °C, 4 h) ceria nanopowders (3 g) were added in 150 mL DI water under stirring. $Cu(NO_3)_2{\cdot}2.5H_2O$ (3.08 mmol, 0.716 g) was dissolved in 75 mL DI water and added into the above CeO_2 solution dropwise. The pH was adjusted at 9 during the whole process by adding freshly made sodium carbonate (Na_2CO_3, 99.5%, Alfa) buffering solution (0.5 M) dropwise. The resulting precipitates were aged at room temperature for 1 h and then filtered, washed three times with DI water at room temperature. The product was dried in vacuum at 70–80 °C overnight, and then air-calcined at 400 °C for 4 h. In all air calcinations, the heating rate was 2 °C/min.

The samples reported here are denoted as *a*CuCe-*b*-(*L*), where *a* is the copper content in atomic percent ($a = [Cu/(Cu+Ce)]_{mol} \times 100$)], and *b* is the preparation method (CP: coprecipitation; Rod: deposition–precipitation on ceria nanorods; Cube: deposition–precipitation on ceria nanocubes). "*L*" stands for samples leached by sodium cyanide (NaCN) solutions [9]. The NaCN-leaching was done in a 2% NaCN–NaOH (pH = 12) aqueous solution at room temperature. An aqueous solution of ammonium carbonate ($(NH_4)_2CO_3$, 2 mol/L) was also used as leaching agent. The NaCN- or $(NH_4)_2CO_3$-leached samples were air-calcined at 400 °C for 4 h prior to testing. Hence, these samples were exposed at 400 °C for twice as long as the corresponding parent samples.

2.2. Characterization

The bulk metal composition in each sample was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin-Elmer, Plasma 40).

The BET specific surface area (*S*) was measured by single-point nitrogen adsorption/desorption measurements at 77 K in 30% N_2/He on a Micromeritics Pulse ChemiSorb 2705 instrument. The as-calcined samples were pretreated in He at 200 °C for 30 min.

The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku RU300 X-ray generator with a 185 mm diffractometer (50 kV, 300 mA) or a Inel XRG 3000 diffractometer (30 kV, 30 mA), using Cu-Kα radiation ($\lambda = 1.5406$ Å). The scan was processed at a rate of 2°/min, and with a step of 0.02° for the former instrument. The lattice constant *a* of cubic Fluorite phase was calculated by least-squares refinement of cell dimensions from powder data, based on Cohen's Method [20,21]. The average grain size (*D*) was estimated according to the Scherrer equation [22], $D = 0.90\lambda/\beta\cos\theta$, where θ is the diffraction angle of the (1 1 1) peak of the cubic Fluorite phase, β is the full width at half maximum (FWHM) of the (1 1 1) peak (in radian), which is calibrated from high purity silica or bulk CeO_2 (5 μm) standard. The microstrain (ε) in the lattice of the as calcined crystallites was estimated by the single line method for analysis of XRD line broadening using a pseudo-Voigt profile function [23].

Transmission electron microscopy (TEM) was conducted on a JEOL 200cx instrument at 200 kV. The TEM samples were prepared by applying a drop of the ethanol suspension containing dispersed catalyst powders onto carbon-coated copper grids. High-resolution TEM (HRTEM) was done on a JEOL 3000F TEM/STEM (300 kV) at the Center for Functional Nanomaterials (CFN), Brookhaven National Laboratory (BNL).

The surface metal ratios of copper to cerium in the studied catalysts were determined by X-ray photoelectron spectroscopy (XPS) in an ion-pumped chamber of Axis Ultra (U.K.) spectrometer equipped with a focused mono-chromatic X-ray source (Al-Kα, $h\nu = 1486.6$ eV). The sample powders were pressed on a copper electric tape for analysis. All the measurements were carried out at room temperature without any sample pre-treatment. The binding energy (*BE*) with a resolution of 0.1 eV was adjusted to the C 1s peaks at 285.0 eV.

The oxidation states of copper in each sample were identified by X-ray absorption near-edge structure (XANES) on the beamline X19A or X18B of National Synchrotron Light Source (NSLS) at BNL. Cu-K edge was investigated, and bulk CuO, Cu_2O and Cu were used as Cu^{2+}, Cu^{+}, and Cu^{0} standards, respectively. Experimental data were collected in the fluorescence mode with a PIPS detector. The X-ray absorption edge energy was calibrated by assigning the 8979 eV to the first inflection point in the standard Cu foil XANES. The *in situ* tests were carried out in a gas mixture of 5% CO/3% H_2O/He.

2.3. Catalytic tests

Temperature-programmed reduction by hydrogen (H_2-TPR) was carried out in a Micromeritics Pulse ChemiSorb 2705 instrument equipped with a thermal conductivity detector (TCD).