

# Effect of additives on the WGS activity of combustion synthesized CuO/CeO<sub>2</sub> catalysts

T. Tabakova<sup>a,\*</sup>, V. Idakiev<sup>a</sup>, J. Papavasiliou<sup>b</sup>, G. Avgouropoulos<sup>b</sup>, T. Ioannides<sup>b</sup>

<sup>a</sup> Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

<sup>b</sup> Foundation for Research and Technology-Hellas (FORTH), Institute of Chemical Engineering and High Temperature Chemical Processes (ICE-HT), P.O. Box 1414, Patras GR 265 04, Greece

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## Abstract

This paper presents a study on the role of additives (samaria, lanthana, zirconia, and zinc oxide) to ceria as a support of copper catalysts for low-temperature WGS. A single-step urea-combustion procedure was used for preparation of highly active catalysts. The results revealed the beneficial role of Sm<sub>2</sub>O<sub>3</sub> and ZnO doping in increasing BET surface area and total pore volume of the catalysts and decreasing the degree of crystallinity of ceria. TPR profiles evidenced enhanced reducibility of modified catalysts. The WGS activity of these catalysts correlates well with BET, XRD, and TPR data. By comparing the catalysts with a commercial CuO–ZnO–Al<sub>2</sub>O<sub>3</sub> sample we point out the feasibility of using CuO/doped-ceria catalysts for low-temperature WGS.

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## 1. Introduction

The water–gas shift reaction (WGS) has a long historical application as an industrially important process for hydrogen production. In the past years, low-temperature WGS has attracted renewed interest due to the increasing demands for high-purity hydrogen for application in fuel-cell systems [1]. Ceria-based WGS catalysts have been studied as an alternative to the commercially available CuO–ZnO–Al<sub>2</sub>O<sub>3</sub> low-temperature catalysts. Ceria is well known as one of the major supports widely applied in the automotive three-way catalytic converter. The high activity of ceria in redox reactions is related to its ability to change from Ce<sup>4+</sup> under oxidizing conditions to Ce<sup>3+</sup> under net reducing conditions and vice versa [2]. Additionally, ceria is known to promote the WGS reaction and to affect the dispersion of supported metals. The promotion by noble or transition metal enhances the ceria reducibility and facil-

itates the generation of very active centers at the interface between metal and support. The WGS has been investigated over ceria-supported precious metals (Pt, Pd, Rh, Ru) [3–6]. Bunluesin et al. have described the WGS mechanism as a redox one and noted the importance of oxygen transfer from ceria to the metal interface and ceria re-oxidation [3]. Very recently, Gorte and Zhao have reviewed the great potential of ceria-supported precious metals for use as WGS catalysts in fuel processors for fuel-cell applications [7]. Currently, Au-ceria catalysts have also been reported as exhibiting very interesting properties for the LT-WGS reaction [8–15]. The availability of nanosized gold particles on the surface in close contact with ceria plays a decisive role for high activity and stability of these catalysts [14]. Fu et al. used sodium cyanide leaching treatment of high-content (2–8 at.%) gold-ceria catalysts and demonstrated that these low-content gold-ceria materials display the same WGS activity as the high-content gold ones [15]. From an economical point of view the attention has been focused on 3d transition metals catalysts [16,17]. Copper is usually preferred as the active component in

\* Corresponding author. Tel.: +359 2 9792528; fax: +359 2 9712967.  
E-mail address: [tabakova@ic.bas.bg](mailto:tabakova@ic.bas.bg) (T. Tabakova).

WGS catalysts because of its high activity at low-temperatures and a cost lower than that of precious metals [16,18–20]. Li et al. have found that copper-ceria catalysts are more stable than other copper-based LT-WGS catalysts and at least as active as the precious metal-ceria catalysts [16]. Doping of ceria by divalent or trivalent ions can increase the concentration of oxygen vacancies or improve its thermal stability. Although WGSR has been studied extensively, there are only several papers on WGS activity of doped-ceria catalysts [16,21–24]. Li et al. have shown that La-doped-ceria retained a small crystallite size (7 nm) and medium high surface area (90–110 m<sup>2</sup>/g) after calcination at 650 °C [16]. Wang and Gorte have demonstrated that the WGS activity of Pd/ceria catalysts can be enhanced by the addition of monolayer coverages of Fe<sub>2</sub>O<sub>3</sub> on ceria, while the addition of monolayer oxides of Tb, Gd, Y, Sn, Sm, Pr, Eu, Bi, Cr, and V to ceria had minimal effect on the reaction rates [21].

Several procedures are described in the literature for preparation of copper-ceria WGS catalysts: urea co-precipitation-gelation [16], impregnation [18], sol-gel [19], co-precipitation or deposition-precipitation [20], and modified reverse microemulsion method [18]. Some of us have previously reported that the urea-nitrates combustion method is an attractive technique for preparation of CuO–CeO<sub>2</sub> catalysts with favorable characteristics and catalytic properties for selective CO oxidation in the presence of H<sub>2</sub> [25]. The combustion synthesis offers several advantages over conventional preparation methods such as low processing cost and simple, solvent-free, and quick preparation route, leading to homogeneous, high surface area materials without the need of additional calcination steps.

The aim of the present study is to investigate the role of different metal oxides as modifying additives to CuO/CeO<sub>2</sub> on the WGS activity of these catalysts. Additionally, a novel single-step urea-combustion method was employed for doping of ceria with Sm, Zn, Zr, and La ions. The results show the capability of this method to produce highly dispersed and active WGS catalysts. Moreover, it could be an alternative route in terms of cost, production rate, and environment.

## 2. Experimental

### 2.1. Catalysts preparation

Doped copper-cerium mixed oxide catalysts were prepared via the urea-nitrate combustion method [25]. Nitrate salts of copper [Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O], cerium [Ce(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O] and metal modifier were mixed with urea [CH<sub>4</sub>N<sub>2</sub>O] in an alumina crucible with the appropriate molar ratios: Cu/(Cu + Ce + M) = 0.15, M/(M + Ce) = 0.05 (where M is the metal modifier added each time, only in the case of Zr the molar ratio Zr/(Zr + Ce) is 0.25), and 75% excess of urea. The mixed solutions were preheated on a hot plate at ~80 °C to remove excess water. The resulting

viscous gel was placed in an open muffle furnace maintained at 400–500 °C. The solution is auto-ignited after a few seconds yielding a voluminous solid product. In order to burn-off any carbonaceous residues, the powders were further heated at 550 °C for 1 h.

### 2.2. Catalyst characterization

The specific surface area ( $S_{\text{BET}}$ ) and the pore volume ( $V_{\text{P}}$ ) of the samples were determined by nitrogen adsorption–desorption at –196 °C using a Quantachrome Autosorb-1 instrument. The specific surface area ( $S_{\text{BET}}$ ) of the samples was calculated following the BET (Brunauer–Emmett–Teller) procedure at six relative pressures of nitrogen in the range of 0.05–0.3. Prior to the measurements, the samples were outgassed at 200 °C for 2 h under vacuum.

The crystalline structure of mixed oxides was analyzed by means of X-ray powder diffractometer (Philips PW1830/40) employing Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm). The X-ray was operated at 40 kV and 30 mA.

Temperature-programmed reduction (TPR) experiments were performed under a flow of a 3% H<sub>2</sub>/He mixture (50 cm<sup>3</sup> min<sup>–1</sup>) over 60 mg of catalyst using a heating rate of 10 °C min<sup>–1</sup>. Prior to TPR, the catalysts were treated under air flow (20 cm<sup>3</sup> min<sup>–1</sup>) at 400 °C for 30 min. A mass spectrometer (Omnistar/Pfeiffer Vacuum) was used for on-line monitoring of TPR effluent gas. The curves in H<sub>2</sub>–TPR profiles correspond to H<sub>2</sub> consumption. These profiles correlate well with the corresponding profiles of H<sub>2</sub>O evolution.

### 2.3. Catalytic activity measurements

WGS activity measurements were carried out in a flow reactor at atmospheric pressure by increasing the reaction temperature step-wise. The reactant gas mixture fed into the reactor contained 4.42 vol% CO, the rest being argon. The following conditions were applied: catalyst bed volume = 0.5 cm<sup>3</sup> (0.63–0.80 mm pellets), space velocity = 4000 h<sup>–1</sup>, partial pressure of water vapor = 31.1 kPa. The analysis of the mixture converted at the reactor outlet was carried out on an “URAS-3G” (Hartmann and Braun AG) gas analyzer with respect to the CO content at every 40 °C step after stationary conversions were achieved. The catalytic activity was expressed by the degree of CO conversion. The catalysts were also studied under different space velocities (2000, 4000, and 8000 h<sup>–1</sup>).

## 3. Results and discussion

### 3.1. Catalyst characterization

The specific surface area of CuO/ceria and CuO/doped-ceria catalysts prepared by the combustion method is reported in Table 1. The modification with samaria and zinc oxide leads to increase of  $S_{\text{BET}}$ , while addition of zirconia and lanthana causes the opposite effect. The

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