



Tungsten as an interface agent leading to highly active and stable copper–ceria water gas shift catalyst

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ABSTRACT

A series of W–Cu–Ce mixed oxide catalysts prepared by microemulsion was evaluated in the water–gas shift (WGS) reaction. At low temperatures (<350 °C), the total conversion of CO on the W–Cu–Ce systems was two times larger than on binary Cu–Ce mixed oxides which are well known catalysts for the WGS. In addition and in contrast with Cu–Ce, W–Cu–Ce catalysts were stable and no signs of deactivation were found after 10 h of reaction time. The rationale for the excellent catalytic performance presented by the W–Cu–Ce ternary oxide was elucidated from the viewpoint of a complete structural (e.g. analysis of the long and short range order) and redox behavior characterization using in situ, time-resolved X-ray diffraction (XRD) as well as X-ray absorption (XAS), infrared (diffuse reflectance Fourier transform DRIFTS) and Raman spectroscopies. From a single phase fluorite-type structure, the catalysts show significant structure/redox evolution under reaction conditions as a function of the W and Cu content. As it occurs in the parent Cu–Ce system, the dominant presence of metallic Cu and fluorite-type oxide phases is detected under reaction conditions for the ternary systems. An outstanding promotion of catalytic properties is nevertheless evidenced for samples with W content above 10 at.% and is shown to be related to the presence of oxidized W–Cu local entities. Such local entities, which are obviously characteristic of the ternary system, greatly enhance fluorite redox properties and play an interfacial role between the main metallic Cu and fluorite-type oxide phases. As a consequence of all these effects, incorporation of W into the initial material leads to efficient WGS catalysts, most promising for their application in the so-called low temperature region, e.g. below 350 °C.

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1. Introduction

Challenges in energy and environmental fields call for the development of highly active and stable catalysts, allowing for more efficient and cleaner processes [1]. The water gas shift reaction (WGS; $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2$) has become a leading technology in the chemical industry, particularly in relation to the production of clean hydrogen and energy recovering systems [2]. In this field, alternatives to Cu–ZnO based systems that may work with reasonable stability at low temperatures, e.g. below 350 °C are actively sought. Ceria-based materials have shown rather interesting properties in WGS during recent years, unveiling thus potential to become real alternatives in the future [2,3].

Cu–CeO₂ systems are among the most active WGS systems and, compared with Pt, Pd, Au and, generally, expensive noble metal based materials, they constitute an interesting alternative from an economical point of view. Among possible different configurations of Cu–CeO₂ materials, Cu–Ce mixed oxides have shown reasonable activity and relatively good stability [4–6]. Due to the different chemical and usually structural properties of doping metals (such as Cu) at Ce-based oxide environments, doping of ceria strongly affects its inherent physico-chemical properties [7]. At a structural level, a dopant can introduce stress into the lattice of an oxide host, inducing in this way the formation of defects to fulfill charge neutrality and modifying chemical reactivity. On the other hand, the lattice of the oxide host can impose on the dopant element non-typical coordination modes with the subsequent perturbation in the dopant chemical properties. Furthermore, the combination of two metals in an oxide matrix can produce materials with novel structural or electronic properties derived either directly from the chemical state of the doping agent and/or by the corresponding charge neutrality defects that can lead to superior catalytic activity or selectivity [4,5,8–14].

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As a general rule, the activity for WGS of systems containing reducible oxides as ceria and “active” species as copper is intimately related to the performance of the copper-ceria interface. Moreover, it appears that highly active ceria-based materials perform dominantly through a redox mechanism, being formate-related mechanisms only of relevance in cases where poor activity is observed [4,15,16]. Furthermore, the presence and capital role of ceria vacancies at copper-ceria interfaces (e.g., a Cu–O vacancy interaction) is well established while the exact Cu active species is more complex to be definitively settled down. The exact chemical state of the system appears however partially (e.g. Cu⁺) or totally reduced (Cu⁰) [4–6,10–13,17]. Cu–CeO₂ seems in any case a rather unique system to define the copper oxidation state as Cu appears to be (partially) reversibly in and out of the fluorite structure in response to the oxidizing or reducing nature of the gas atmosphere with a concomitant change in oxidation state. This behavior has been only observed up to now for Cu and Pd (and possibly Pt) at the Ce-fluorite solid solutions [4,12b,18,19,20]. In any case, this quasi-free state of copper may explain the difficulty in getting a definitive assignment of the Cu active species in several chemical reactions like CO oxidation, CO preferential oxidation, water gas shift, etc.

The quest of improving chemical activity of Cu–Ce requires the development of novel, advanced materials. In this work we investigate the effect of tungsten introduction on a Cu–Ce mixed oxide matrix for the WGS reaction upon formation of a ternary mixed oxide. Our findings indicate that the rich chemistry of Cu in a ceria matrix and its inherent potential in the WGS reaction through Cu–Ce interfaces [3–6,10–14,21] can be modulated by the presence of a third species, in this case W. We will show here that tungsten addition to the catalyst formulation renders a highly active and stable catalyst, particularly in the low temperature region, below 350 °C. To this end, an in situ study of the W–Cu–Ce system behavior under WGS was carried out with the help of synchrotron-based X-ray diffraction (XRD) and absorption (XAS) techniques, complemented with vibrational infrared and Raman spectroscopic tools. The analysis indicates that W affects both the cerium and the copper components but key elements are related to the formation of W–Cu local entities which definitively modulate the redox behavior of the ceria phase in reaction conditions.

2. Experimental

2.1. Sample preparation

The W–Cu–Ce catalysts were prepared by employing reverse microemulsions containing n-Heptane, Triton-X-100 and n-Hexanol as organic solvent, surfactant and cosurfactant, respectively, in amounts similar to those reported previously [4,22]. The required amount of ceria nitrate (Aldrich) copper nitrate (Aldrich) and ammonium tungsten oxide (Aldrich) was dissolved in distilled water and dispersed within already mentioned organic components to form the reverse microemulsion. Simultaneously, another microemulsion of similar characteristics was prepared containing dissolved in its aqueous phase the required amount of tetramethyl ammonium hydroxide (TMAH). After 1 h stirring of the two microemulsions, the TMAH-containing one was added to the metal-containing one and it was left for the period of 18–24 h in order to complete the precipitation reaction. The resulting solid was then separated by centrifugation and decantation, rinsed with methanol, dried overnight at 100 °C and the resulting powder was calcined at 500 °C for 2 h under air. Similar reference Cu–Ce, W–Ce and Ce systems were obtained by the same method. Chemical compositions were analyzed by ICP-AES and correspond to the ones mentioned in samples names in Table S1 (supporting information)

within a maximum error of ±2 at.%. Table S1 also displays the BET specific surface areas of the materials.

2.2. Catalytic measurements

The catalysts were tested in a quartz tubular catalytic reactor for their activity under an atmospheric pressure flow (using mass flow controllers to prepare the reactant mixture except for water which was injected in a warm line using a syringe pump) of 3% CO, 3% H₂O (Ar balance), with a total flow of ca. 100 mL min⁻¹ (roughly corresponding to 42,000 h⁻¹ GHSV). Catalytic runs were followed using a mass spectrometer (Pfeiffer Omnistar 300) and Gas Chromatography (GC-2014 Shimadzu). Tests were carried out in the 200–450 °C interval at 50 °C steps, maintaining the reaction temperature at each plateau up to quasi-steady state equilibrium (typically 30–60 min). Additional tests were used to ensure the absence of methanation, CO preferential oxidation, or other possible side reactions. This was checked by the exclusive presence of H₂ and CO₂ products in the correct stoichiometric quantities. Finally, stability isothermal tests were run at 300 °C.

2.3. X-ray diffraction

In situ time-resolved X-ray diffraction (TR-XRD) experiments were carried out on beam line X7B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) using an excitation energy of ~38.8 KeV ($\lambda = 0.3196 \text{ \AA}$). The sample (~5 mg) was loaded into a glass or quartz reactor of 1 mm diameter, which was attached to a flow system [23,24]. A small resistance heater was wrapped around the capillary, and the temperature was monitored with a 0.5 mm chromel–alumel thermocouple placed in the capillary near the sample. Two-dimensional powder patterns were collected with a Perkin-Elmer image plate detector and the powder diffraction rings were integrated using the FIT2D code [25]. The instrument parameters (Thompson-Cox-Hastings profile coefficients) were derived from the fit of a LaB₆ reference pattern. Rietveld profile refinements were performed with the aid of GSAS software [26,27]. The series of powder patterns were refined by sequential analysis where the starting model is based on the earlier powder pattern. Diffraction patterns were collected over the catalyst during the WGS reaction or several specific atmospheres containing H₂O or CO. Similarly to the catalytic test, the WGS reaction was carried out with a stepped temperature program from room temperature to 400 °C, with 2 h soaks at every 100 °C beyond 200 °C amid a 3% CO, 3% H₂O (He balance) gas mixture flow rate of 10 mL min⁻¹ at a space velocity of 42,000 h⁻¹. Additional isothermal experiments were carried out at 300 °C by subjecting the sample to different atmospheres and obtaining quasi-equilibrium states.

2.4. XAFS

Cu K-edge and W L₃-edge in situ near-edge (XANES) and extended (EXAFS) absorption fine structure spectra were collected at beamline X18A and X19A of the NSLS at BNL under similar operational conditions as those for the catalytic and TR-XRD experiments. The same cell was used for the XAS experiments as that for in situ XRD, except that the sample was loaded into a Kapton tube (I.D. = 1/8 inch). The X-ray absorption spectra were taken repeatedly in the “fluorescence-yield mode” using a passivated implanted planar silicon (PIPS) detector cooled with circulating water. Due to the strong Ce-related fluorescence background, useful EXAFS data were only acquired at room temperature after maintaining the systems in WGS at 300 °C for 1 h and cooling down in the same testing atmosphere. The XANES and EXAFS data were then analyzed using the Athena [28,29] and VIPER (www.dessy.de/klmn/viper.html)

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