



Review article

The role of Copper–Ceria interactions in catalysis science: Recent theoretical and experimental advances

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ARTICLE INFO

Article history:

Received 19 March 2016
 Received in revised form 13 May 2016
 Accepted 18 May 2016
 Available online 20 May 2016

Keywords:

Cu–Ceria interactions
 Metal–support interface
 Electronic Metal Support Interactions (EMSI)
 Operando techniques
 DFT calculations
 Inverse catalysts
 Methanol synthesis
 WGS
 PROX
 N₂O decomposition

ABSTRACT

Copper-containing cerium oxide materials have received considerable attention both in catalysis and electro-catalysis fields due to their unique physicochemical characteristics in conjunction to their lower cost compared to noble metals (NMs)-based catalysts. Nowadays, it is well documented that the complex Copper–Ceria interactions (either geometric or electronic) have a key role on the catalytic performance. Hence, considerable efforts have been devoted on the understanding and the fine-tuning of metal–oxide interactions. Despite the growing progress in the field, several crucial issues related to the influence of: i) particle's shape and size, ii) active site's chemical state, iii) charge transfer between interfacial sites, and iv) intrinsic defects (e.g., surface oxygen vacancies) on the interfacial activity are still under investigation. This survey summarizes the recent advances in the last 10 years on the fundamental origin of Copper–Ceria interactions and their implications on the catalytic activity. The insights lately obtained by means of: i) *ex situ* advanced characterization techniques, ii) *in situ* sophisticated studies (e.g., *operando* techniques), iii) theoretical analysis (e.g., DFT calculations), and iv) innovative probing approaches (such as the inverse CeO₂/CuO model system) are provided. The state-of-the-art catalytic applications of CuO/CeO₂ binary oxides (water gas shift (WGS) reaction, preferential oxidation (PROX) of CO, CO₂ hydrogenation, selective catalytic reduction (SCR), N₂O decomposition, etc.) in relation to the aforementioned aspects are discussed. Some guidelines towards the fine-tuning of the surface chemistry of CuO/CeO₂ catalysts for real life energy and environmental application are provided.

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1. Introduction

In 1993 Soria et al. [1] reported on the significant interactions between CeO₂ and metal ions deposited on its surface, by employing electron paramagnetic resonance (ESR) spectroscopic studies. They proposed that the formation of oxygen vacancies on the CeO₂ surface facilitated the incorporation of Cu²⁺ ions to the support, whereas at elevated temperature a deeper chemical interaction is produced, which is followed by the agglomeration of copper with a ferromagnetic-type behavior. Later on, Liu and Flytzani-Stephanopoulos [2] introduced the CuO/CeO₂ system for the catalytic oxidation of CO and CH₄. An extraordinary catalytic activity was recorded, attributed to the strong interaction between the copper and the fluorite-type oxide carrier. Following these pioneering studies more than 1500 articles have been published in relation to the catalytic performance of CuO/CeO₂ catalysts and its origin.

Nowadays, materials consisting of copper and ceria are employed in a wide variety of energy and environmental applications due to their unique catalytic features and lower cost as compared to NMs-based catalysts. In particular, CuO/CeO₂ catalysts have shown great potential as alternatives to NMs for many catalytic applications, involving among others: oxidation of volatile organic compounds (VOCs), water–gas shift (WGS) reaction, low temperature CO oxidation, preferential oxidation of CO in the presence of H₂ excess (CO-PROX), CO₂ hydrogenation toward methanol synthesis, steam reforming (SR) of alcohols/hydrocarbons, selective catalytic reduction (SCR) of NO_x, soot oxidation and nitrous oxide (N₂O) decomposition. Moreover, CuO/CeO₂ catalysts have been widely employed as anode composites in solid oxide fuel cells (SOFCs) due to their adequate electronic conductivity, sufficient electrochemical activity and their resistance to coke formation. Several comprehensive review articles have been already devoted on the applications of CuO/CeO₂ catalysts [3–6]. In this regard, the aim of the present review is to exemplify the fundamental origin of the synergistic metal–support interactions, based on the recent experimental and theoretical advances in the field. Table 1 depicts at a glance the most common applications of CuO/CeO₂ binary system in heterogeneous catalysis along with the commonly considered implications of Cu–Ceria interactions in relation to each process.

Due to the broad range of applications of CuO/CeO₂ catalysts it is of paramount importance to gain further insight into the fundamental understating of Cu–Ceria interactions and their consequences on the catalytic performance. It has been postulated that the intimate contact between CuO and CeO₂ is of essential importance in explaining the remarkable performance of CuO/CeO₂ composites for the aforementioned applications. Moreover, the increasing interest in CuO/CeO₂ system has triggered a substantial research from the theoretical point of view [102,105,119–129]. Nevertheless, the determination of active sites surface structure still consists a challenging task, due to the formation of different interacting species, solid solutions, surface defects (e.g., oxygen vacancies) and electronic perturbations that could coexist in complex supported metal systems under real working conditions.

In the light of the above aspects, the present study aims to shed some light on the fundamental origin of Cu–Ceria interactions and their particular effect on the catalytic performance. Under this perspective, the recent advances lately obtained by means of *in situ* or *ex situ* characterization techniques, theoretical studies and innovative probing approaches (such as the inverse CeO₂/CuO model system) will be presented. The state-of-the-art applications of CuO/CeO₂ catalysts in relation to the above aspects will be outlined. To gain exclusively insight into Cu–Ceria interactions the present review is limited on the studies related to the binary sys-

tem CuO–CeO₂, ignoring the doping effects that can be induced by various aliovalent modifiers.

2. Copper–Ceria interactions: from SMSI to EMSI?

Cerium oxide or ceria (CeO₂) has been long received increasing attention as a key component in three-way catalytic converters, solid oxide fuel cells, as well as in many industrial and environmental catalytic applications. The wide range of ceria applications can be attributed to its peculiar capability, associated with the Ce⁴⁺/Ce³⁺ redox cycle, to act as an “oxygen buffer” by storing and releasing oxygen under oxidizing and reducing conditions, respectively. More interestingly, many literature studies clearly revealed that the exceptional redox properties of CeO₂ can be further tuned by an appropriate combination with precious and base metals, especially with copper [6,130–134].

It has been well documented that CuO/CeO₂ catalysts demonstrated specific activities comparable or even better to precious metal catalysts for several processes, such as CO oxidation [38], CO-PROX reaction [13], N₂O decomposition [135], etc. The superior reactivity of CuO/Ceria catalysts has been in principle correlated with a synergistic effect linked to strong Copper–Ceria interactions. Several interrelated factors are usually regarded under the general umbrella of “synergism” in order to explain the superiority of CuO/Ceria binary system, involving among others:

- (i) the facilitation of redox interplay between Cu²⁺/Cu⁺ and Ce³⁺/Ce⁴⁺ redox couples [136];
- (ii) the presence of defects, such as oxygen vacancies [107,119,131,137,138];
- (iii) superior reducibility of mixed CuO–Ceria composites as compared to that of individual counterparts [107,131,139];
- (iv) the geometric or ligand effects induced by the interaction of metal with the support [136];
- (v) the interfacial reactivity, *i.e.*, the unique activity which give rises at the metal–support interface [136].

In the majority of the studies devoted to CuO/Ceria catalysts, one or more of the abovementioned factors were accounted for their enhanced catalytic activity, without providing, however, the underlying mechanism of these effects. The complexity of the Copper–Ceria interactions in conjunction to the limited availability of *in situ* sophisticated techniques notably hinders the mechanistic understanding at atomic level [140]. Hence, the present review aims to gain insight into the nature and the extent of these interactions based on the state-of-the-art theoretical and experimental studies, which have been obtained in the last years. In the following paragraphs the latest advances regarding the nature of metal–support interactions are summarized.

In relation to the impact of support on the catalytic activity it has been presumed for a long time that supporting carriers, involving reducible oxides, are “inert” materials, providing simply the basis for active phase dispersion. Nowadays, however, it has been well documented – thanks to the rapid development of new generation theoretical and experimental tools – that support is no longer “innocent”. It is now known that metal oxide carriers have a profound influence on the surface properties, which is reflected on catalytic activity [133,136,141,142].

In recent studies by author and co-workers [77,91,143], devoted on the influence of support on the surface and redox properties of Cu-based catalysts, it was revealed that CuO supported on CeO₂ demonstrated the optimum reducibility amongst a series of bare or mixed rare earth oxides (REOs)-based carriers (Fig. 1). More specifically, it was found that the amount of H₂ consumed in Cu catalysts supported on non-reducible carriers, such as Sm₂O₃ and

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