

Catalytic processes during preferential oxidation of CO in H₂-rich streams over catalysts based on copper–ceria[☆]

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Abstract

Nanostructured catalysts based on combinations between oxidised copper and cerium entities prepared by two different methods (impregnation of ceria and coprecipitation of the two components within reverse microemulsions) have been examined with respect to their catalytic performance for preferential oxidation of CO in a H₂-rich stream (CO-PROX). Correlations between their catalytic and redox properties are established on the basis of parallel analyses of temperature programmed reduction results employing both H₂ and CO as reactants as well as by XPS. Although general catalytic trends can be directly correlated with the redox properties observed upon separate interactions with each of the two reductants (CO and H₂), the existence of interferences between both reductants must be considered to complete details for such activity/redox correlation. Differences in the nature of the active oxidised copper–cerium contacts present in each case determine the catalytic properties of these systems for the CO-PROX process.

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1. Introduction

Production of H₂ for polymer fuel cells (PEMFC) is usually accomplished by a multi-step process that includes catalytic reforming of hydrocarbons or oxygenated hydrocarbons followed by water gas-shift (WGS) [1,2]. The gas stream obtained after these processes presents in most cases a relatively high CO concentration that disallows efficient handling of the fuel by the Pt alloy anode usually employed in the PEMFC. Preferential (or selective) oxidation of CO (CO-PROX process) has been recognized as one of the most straightforward and cost-effective methods to achieve acceptable CO concentrations (below ca. 100 ppm) [3–8]. Among different types of catalysts that have shown their ability for this process (including those based on Pt and Au), a group constituted by catalysts based on closely interacting copper oxide and ceria (or structurally related

ceria-containing mixed oxides) has shown promising properties in terms of activity, selectivity and resistance to CO₂ and H₂O, while their lower cost could make them strongly competitive [3,4,6,7,9–15].

The particular ability of the latter class of catalysts for the CO-PROX or related processes has been essentially attributed to the synergistic redox properties in the presence of copper–ceria interfacial sites [4,6,10,11,16–21]. Previous work from our group was dedicated to analyse differences in the CO-PROX catalytic performances as a function of the support employed in a series of CuO/(Ce,M)O_x (with M = Zr or Tb) catalysts [11]. In agreement with studies of a similar type [9,22,23], it was shown that the CuO/CeO₂ configuration yielded best results in terms of both CO conversion and CO-PROX selectivity, which was generically attributed to the higher interfacial redox activity of such catalyst [11]. Selectivity differences between the catalysts could be related to structural/morphological properties of the copper oxide species present in each case [11]. Nevertheless, details are lacking with respect to the nature of the processes involved in the reaction mechanism and/or their respective evolutions during the catalytic process [6,10,16]. Generally speaking, the properties of

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