

Preferential oxidation of CO in a H₂-rich stream over CuO/CeO₂ and CuO/(Ce,M)O_x (M = Zr, Tb) catalysts

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Abstract

Catalysts with the same copper oxide loading supported on cerium oxide and Ce–M (M = Zr or Tb) mixed oxides are examined with respect to their performance for preferential oxidation of CO (CO-PROX) in a H₂-rich stream. The catalytic activity results are analysed in combination with *operando*-DRIFTS tests done under similar conditions and characterization results obtained by XRD, XPS and XAFS techniques. The presence of essentially highly dispersed CuO entities strongly interacting with the corresponding supports and differing in their dispersion degree is evidenced by these techniques. The catalytic activity results reveal significant support effects affecting the conversion of either CO or H₂ as well as the selectivity for the CO-PROX process. These are explained on the basis of differences in the interfacial redox activities of the corresponding copper oxide-support contacts, while copper oxide particle size effects are proposed to be relevant to explain overall CO-PROX selectivities obtained.

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1. Introduction

Hydrogen production from hydrocarbons has been proposed as the most efficient process to obtain such fuel for its use by proton-exchange membrane fuel cells (PEMFC). However, the gas produced after reforming of hydrocarbon fuels followed by water gas-shift (WGS) processes employed for this purpose still presents in most cases (typical composition: 45–75 vol.% H₂, 15–25 vol.% CO₂, 0.5–2 vol.% CO, a few vol.% H₂O and traces of unconverted fuel [1]), 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 (PROX process) has been recognized as one of the most straightforward and cost-effective methods to achieve acceptable CO concentrations (below ca. 100 ppm) [1–4].

Different types of catalysts have shown their efficiency for the PROX process. These can be classified into three general groups as a function of their nature and/or consequent catalytic properties. The first one involves supported noble metal catalysts (mainly Pt ones) and follows from first developments done by Engelhard researchers in the context of processes related to ammonia production [1,5]. Although nowadays operating PROX systems include this type of catalysts, they present the main drawback (apart from their cost) of their relatively low selectivity for the process (that could probably be enhanced with the use of certain promoters and/or upon appropriate selection of the support [6,7]) at their operating temperature (between 423 and 473 K), which makes necessary including interstage cooling operations to avoid extensive heating as a consequence of the exothermicity of the reactions involved [1,8]. A second group involves supported gold (or oxidized gold) catalysts, well known for their outstanding performance for CO oxidation [1,9,10]. These systems show a high activity for the PROX process

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