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Selective oxidation of CO in H_2-rich stream over Au/CeO_2 and Cu/CeO_2 catalysts: An insight on the effect of preparation method and catalyst pretreatment

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ABSTRACT

Selective oxidation of CO in H_2-rich stream was studied on Au/CeO_2 and Cu/CeO_2 catalysts, investigating the effect of both the preparation technique and the catalyst pretreatment towards the catalytic performance. It was found that in the case of Au catalysts the sample prepared by deposition–precipitation was more active than that prepared by co-precipitation. The opposite trend was instead observed on Cu samples. On all tested catalysts a higher pre-calcination temperature of catalysts resulted in a lower CO conversion. The extent of this effect was strong on Au samples and less evident on Cu ones. On both Au and Cu samples selectivity towards CO oxidation decreased on increasing reaction temperature, being almost independent from preparation and pretreatment. On the basis of characterisation data (H_2-TPR, XRD, XPS, and BET surface area) the effect of preparation method and catalyst pretreatment was accounted for both the different particle size and surface amount of active species (Au or CuO_x). According to a Mars-van Krevelen mechanism, implying lattice oxygens of the cerium oxide and CO (and H_2) adsorbed on the active species, it was suggested that on Au/CeO_2 the PROX reaction is strongly affected by the status of gold, which has a key role in the CO activation step, whereas on Cu/CeO_2 the performance are significantly influenced by the ceria morphology/reactivity.

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells are currently considered among the most advanced systems for energy production starting from hydrogen [1]. For this application H_2 stream must be almost free of CO (CO < 50 ppm), in order to avoid poisoning of the Pt anode catalyst [2]. When H_2 is produced by steam reforming of hydrocarbons or alcohols followed by water gas shift reaction, it still contains 0.3–1% of CO, thus requiring further purification. Selective oxidation of CO in H_2-rich stream (known as PROX reaction, PReferential OXidation of carbon monoxide) is one of the most investigated technology for reducing CO concentration to acceptable levels [3–5]. Several catalysts have been considered for PROX, such as oxide supported Pt [6–11], Ru [6,10], Rh [6,12], Ir [11], Pd [6,10] and more recently Au [13–31] and Cu [32–38]. The influence of the nature of the metal oxide support on the PROX activity of supported catalysts has been extensively studied, chiefly on gold catalysts. A wide range of metal oxide supports, such as Al_2O_3 [13–18], Fe_2O_3 [16,17,19–21], TiO_2 [16–18], CeO_2 [16,17,23–25,27–38], CoO_x [16,17,29], MnO_x [16,17,26], NiO_x [16,17], SnO_2 [16,17], ThO_2 [22], ZrO_2 [18] have been reported in the literature.

In the last years CeO_2 has been widely employed as oxidation system due to the so-called oxygen storage capacity (OSC), consisting in the ability to take up oxygen under oxidizing conditions and releasing it under reducing ones [39]. In particular gold supported on ceria has been reported to be among the most active systems for volatile organic compounds (VOCs) combustion [25,40], PROX [23,25,27–31] and low temperature water–gas shift reactions [41]. Cu/ceria catalysts were also found promising for PROX [25,35] and water gas shift [42].

A couple of years ago we reported that the performances of Au/iron oxide towards PROX reaction are strongly dependent from pretreatment conditions of catalysts [21]. Following these considerations we here report a study on the PROX reaction on cerium oxide supported Au and Cu catalysts, focusing on the effect that the preparation method and the catalyst pretreatment play on the CO removal efficacy (activity, selectivity and stability) of catalysts.

2. Experimental

2.1. Catalyst preparation and testing

Cerium oxide supported Au and Cu catalysts were prepared by deposition–precipitation (DP) or co-precipitation (CP), using

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