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Study of CuO/CeO_2 catalyst with for preferential CO oxidation reaction in hydrogen-rich feed (PROX-CO)

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ABSTRACT

The CuO/CeO_2 system was investigated as a catalyst for preferential CO oxidation reaction in hydrogen-rich feed (PROX-CO). The catalysts were prepared by deposition–precipitation (DEP) and co-precipitation (COP) methods and the catalytic performance reveals that the preparation method influences the properties of solids prepared, where a direct consequence is the difference in behavior of the catalysts in the PROX-CO reaction. A high specific area and a better dispersion of the metallic phase were obtained in the catalyst prepared by co-precipitation. The redox properties during the reaction were reported by measures of temperature programmed reduction (TPR), OSC measurements and X-ray absorption near edge structure (XANES-TPR) *in situ* showed the relationship between the preparation method, the physicochemical characteristics and redox properties in the PROX-CO reaction. By this means, the good dispersion of CuO and the best oxygen capacity are the response of the high performance of CuO/CeO_2-COP catalysts for the PROX-CO reaction.

1. Introduction

The CuO/CeO_2 system has been extensively studied for application in preferential CO oxidation (PROX-CO), water–gas shift (WGS) reaction and steam and oxidative reforming of methanol [1–4]. The PROX-CO and WGS reactions are identified as efficient ways to purify hydrogen produced by steam reforming of hydrocarbons and alcohols for application in proton exchange membrane fuel cell (PEMFC).

The good quality results observed in the use of copper catalysts supported on ceria in these reactions are pointed out as a result of the high mobility of oxygen in ceria creating oxygen vacancies, favoring the redox properties of copper. In addition, in this system, the high dispersion of metallic copper is favored by the presence of ceria and there is a strong metal-support interaction and this effect is maximized when CeO_2 is in form of nanoparticles [2,5–10].

The performance of these catalysts depends on the preparation method, since this has an influence on the physicochemical characteristics of solid, affecting the redox couples Cu(I)/(II) and Ce(III)/(IV) and these properties have large influence on the activity of CuO/CeO_2 system in oxidation reactions. The proposed mechanism for PROX-CO reaction with the CuO/CeO_x catalyst is redox type, where one of the steps involves the oxygen from the surface which is removed by a reducing gas (CO or H_2), thus forming an oxygen vacancy [1,2,8,11,12].

The preparation routes most commonly cited in the literature are co-precipitation, deposition-precipitation, impregnation, sol–gel method, urea nitrate combustion, urea gelatination, solution combustion method and chelating method [1,7,9,13–16]. Most traditional methods of synthesis result in a catalyst with low surface area and low dispersion of the metal in the support, besides being morphologically heterogeneous, disadvantaging the main desirable features of the system CuO/CeO_2 for PROX-CO reaction [2,12]. Several methods have emerged as a way of adapting traditional synthesis methods in an attempt to obtain better results.

Djinovic et al. [2] compared CuO/CeO_2 catalysts prepared by co-precipitation and hard template methods. The results showed that the catalysts obtained by hard template method have specific area of approximately 147, 166 and 161 $m^2\,g^{-1}$, respectively, for the metal content of 10, 15 and 20%, and surface area of 22, 54 and 31 $m^2\,g^{-1}$ for the catalysts prepared by co-precipitation method [2]. Liu et al. [7] tested CuO/CeO_2 catalysts prepared by co-precipitation, chelating, citric acid and critical phase methods. The catalyst prepared by chelating showed better catalytic performance, with CO conversion of about 95% at 100 °C, while

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