

Catalytic properties of monometallic copper and bimetallic copper-nickel systems combined with ceria and Ce-X (X = Gd, Tb) mixed oxides applicable as SOFC anodes for direct oxidation of methane[☆]

A. Hornés^a, D. Gamarra^a, G. Munuera^b, J.C. Conesa^a, A. Martínez-Arias^{a,*}

^a Instituto de Catálisis y Petroleoquímica, CSIC, C/Marie Curie 2, Campus de Cantoblanco, 28049 Madrid, Spain

^b Departamento de Química Inorgánica e Instituto de Ciencia de Materiales (Centro Mixto Universidad de Sevilla-CSIC), 41092 Sevilla, Spain

Available online 6 February 2007

Abstract

The present contribution analyses the possibilities of both Cu and bimetallic Cu-Ni formulations combined with CeO₂-based oxides for their use as anodes of solid-oxide fuel cells (SOFC) for direct oxidation of methane. The main objective is related to examining how the metals combination and the presence of dopants like Gd and Tb into the ceria structure could affect the catalytic activity of this type of materials towards reaction with methane. For this purpose, cermets of Cu alone as well as bimetallic Cu-Ni (with 20 and 40 wt.%) have been synthesised in combination with various supports composed by oxides of Ce, Ce-Tb and Ce-Gd. The behaviour of such systems towards interaction with dry methane up to 900 °C was analysed by means of CH₄-TPR tests. Appreciable differences in the catalytic activity are revealed as a function of the presence of nickel as well as Gd or Tb dopants in the systems. The characteristics of carbonaceous deposits formed upon such interaction was analysed by means of TPO and XPS.

© 2007 Elsevier B.V. All rights reserved.

Keywords: SOFC; Anode; Direct oxidation of methane; Intermediate temperature; Copper; Nickel; CeO₂; CGO; Ce-Tb mixed oxide

1. Introduction

Solid oxide fuel cells (SOFC) are galvanic devices most interesting from environmental and energetic points of view due to their high efficiency for conversion from chemical to electrical energy and their high versatility towards employment of various types of fuels [1]. Classical systems of this type involve the employment of thin YSZ electrolytes with an anode based on Ni-YSZ cermets and can attain an energetic efficiency close to 70% operating at relatively high temperature (800–1000 °C) with hydrocarbon reforming mixtures as fuel [1–3]. This efficiency can be theoretically increased by employing direct hydrocarbon oxidation conditions instead of fuel mixtures resulting from reforming [4]. However, the classical anode of nickel could easily be deactivated under those conditions as a consequence of the formation of carbonaceous deposits due to the relatively good activity of

nickel for hydrocarbon cracking [5–8]. Different alternatives were developed in this respect to overcome such deactivating effect. Murray et al. successfully operated a cell on dry methane by employing a nickel-containing ceria-based anode at relatively low reaction temperature (650 °C) [6]. In turn, such ceria-containing anode could in principle be compatible with electrolytes able to operate at intermediate temperatures (500–700 °C) like gadolinium-doped ceria (CGO) [1]. However, the nickel-based anode can be limited when less refractory (and therefore more easy to be cracked) hydrocarbons are employed as fuel [5,7,8].

A more versatile alternative was developed by Gorte, Vohs and col. and consisted in employing anodes including mixtures between copper and cerium oxide [5,7,9–16]. Such configuration has demonstrated to be able to employ a large diversity of hydrocarbon fuels (methane or longer chain ones and even aromatics) under direct oxidation conditions and displaying a reasonable stability [4,7,11]. However, the copper anode can present several limitations related to its relatively low melting temperature, which can make difficult the fabrication of Cu cermets and can also affect the anode stability when operating at high temperature [16,17] (although it could perform

[☆] This paper presented at the 2nd National Congress on Fuel Cells, CONAP-PICE 2006.

* Corresponding author. Tel.: +34 91 585 4940; fax: +34 91 585 4760.

E-mail address: amartinez@icp.csic.es (A. Martínez-Arias).