Available online at www.sciencedirect.com

Applied Catalysis B: Environmental 65 (2006) 207–216

APPLIED CATALYSIS B: ENVIRONMENTAL

www.elsevier.com/locate/apcatb

Preferential oxidation of CO in rich H_2 over CuO/CeO_2: Details of selectivity and deactivation under the reactant stream

A. Martínez-Arias [a,*], A.B. Hungría [a], G. Munuera [b], D. Gamarra [a]

[a] *Instituto de Catálisis y Petroleoquímica, CSIC, C/Marie Curie, Campus Cantoblanco, 28049 Madrid, Spain*
[b] *Departamento de Química Inorgánica, Universidad de Sevilla, 41092 Sevilla, Spain*

Received 19 October 2005; received in revised form 23 December 2005; accepted 9 February 2006
Available online 15 March 2006

Abstract

A CuO/CeO_2 catalyst is examined with respect to its performance for preferential oxidation of CO in H_2-rich streams. Catalytic activity results are explained on the basis of characterization by *operando*-DRIFTS and complemented with the analysis of redox properties by electron paramagnetic resonance (EPR) and X-ray photoelectron spectra (XPS). General catalytic activity features are accounted for by comparative analysis of the activities for individual CO and H_2 oxidation, for which similar CuO and CeO_2 interfacial active sites appear to be involved. An interesting particularity is related to observation of a low temperature hydrogen oxidation process in which CO apparently acts as gaseous promoter. A deactivation process taking place rapidly under the reactant stream is evidenced and attributed to accumulation of hydroxyls on the interfacial active sites and/or to copper sintering in the course of the run.

Keywords: CuO catalyst; CeO_2; CO-PROX; Hydrogen; *Operando*-DRIFTS; XPS; EPR

1. Introduction

Production of H_2 for polymer fuel cells (PEMFC) is usually accomplished by a multistep process that includes catalytic reforming of hydrocarbons or oxygenated hydrocarbons followed by water–gas shift (WGS) [1,2]. However, the gas stream obtained after these processes still presents in most cases (typical composition: 45–75 vol.% H_2, 15–25 vol.% CO_2, 0.5–2 vol.% CO, some vol.% H_2O and traces of unconverted fuel [3]) 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].

Different types of catalysts have shown their efficiency for the CO-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 [9]. They present the main drawback (besides their cost) of their relatively low selectivity for the process at practical operating temperature (between 423 and 473 K), which can make necessary including interstage cooling operations to avoid extensive heating as a consequence of the exothermicity of the oxidation reactions involved [3,10]. A second group of active catalysts involves supported gold catalysts, well known for their outstanding performance for CO oxidation [3,11–13]. These show a high activity for the CO-PROX process with a good match between their activity window and the PEMFC anode operating temperature (353–403 K). They can present however the drawback of their poor resistance to the presence of CO_2 in the reactant mixture [3,12,13]. The third group is constituted by catalysts based on closely interacting copper oxide and ceria (or structurally related cerium-containing mixed oxides), which have shown promising properties in terms of activity, selectivity and resistance to CO_2 and H_2O, while being also most interesting from an economical point of view [3,5–7,14–18].

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 achieved by CuO-CeO_2 interfacial sites [5,6,15,16,19,20]. The correlation observed

---

* Corresponding author. Tel.: +34 915854940; fax: +34 915854760.
E-mail address: amartinez@icp.csic.es (A. Martínez-Arias).

0926-3373/\$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcatb.2006.02.003

between redox and catalytic properties of the system appears a strong indication of operation under a Mars–van Krevelen type mechanism, as also supported by kinetic measurements [6,15,19]. However, within such general kinetic scheme [21], details still lack concerning the nature of the species or processes involved in the reaction mechanism and/or their respective evolutions during the catalytic process [6,15,19], while aspects related to apparent selectivity changes during the course of the reaction or to the deactivation produced under the reactive atmosphere are still under debate [6,7,15].

A 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 [16]. In agreement with studies of a similar type [14,22,23], it was shown that the CuO/CeO_2 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 [16]. In turn, selectivity differences between the catalysts were proposed to be mainly related to structural/morphological properties of the copper oxide species present in each case [16]. As a continuation of that work, the present work aims to get further insights into the catalytic properties of such CuO/CeO_2 catalyst for CO-PROX. Focus will be put in this case on analysing the nature and properties of active centres in the light of a recently proposed model for redox properties of the CuO/CeO_2 catalyst under study [20]. In addition, the origin of a maximum in the CO-PROX selectivity (as reported by different groups [15,16]) and deactivating effects produced upon interaction with the reactant mixture will be addressed. For this purpose, the catalytic performance for the CO-PROX process is analysed mainly by *operando*-DRIFTS spectroscopy, while EPR and XPS are employed to study redox properties of the system. Detailed characterization of the catalyst, presented in previous contributions [16,20], is employed as a basis for the various analyses performed in this work.

2. Experimental

The CeO_2 support was prepared by precipitation within a reverse microemulsion. For this, two microemulsions of similar characteristics containing aqueous phases prepared by dissolving nitrate salt of Ce for the first and tetramethylammonium hydroxyde pentahydrate for the second were mixed; *n*-heptane was used as organic solvent, Triton X-100 (Aldrich) as surfactant and hexanol as co-surfactant in the microemulsions. Following centrifugation, decanting and rinsing of the resulting solid with methanol, it was dried at 383 K for 24 h and finally calcined under air at 773 K for 2 h. Details of the preparation parameters employed during the synthesis of this support can be found elsewhere [16,24]. The supported copper oxide catalyst was prepared by incipient wetness impregnation of the CeO_2 support using an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (to give a final copper load of 1 wt.%, representing ca. 157 μmol of Cu per gram of catalyst). The resulting material was dried overnight at 383 K and subsequently calcined under air at 773 K for 2 h.

The CuO/CeO_2 catalyst calcined in situ (under oxygen diluted in nitrogen at 773 K) was tested in a glass tubular catalytic reactor for its activity under an atmospheric pressure flow (using mass flow controllers to prepare the reactant mixture) of 1% CO, 1.25% O_2 and 50% H_2 (Ar balance), at a rate of $1 \times 10^3\ cm^3\ min^{-1}\ g^{-1}$ (roughly corresponding to $80{,}000\ h^{-1}$ GHSV) and using a heating ramp of $5\ K\ min^{-1}$ up to 573 K; at the end of the test, the catalyst was examined during cooling under the same flow using a $-5\ K\ min^{-1}$ ramp in order to check possible deactivation effects. Analysis of the feed and outlet gas streams was done by gas infrared (Perkin-Elmer FTIR spectrometer model 1725X, coupled to a multiple reflection transmission cell; Infrared Analysis Inc. "long path gas minicell", 2.4 m path length, ca. 130 cm^3 internal volume) while a paramagnetic analyser (Servomex 540 A) was used to analyse the O_2 concentration. No products other than those resulting from CO or H_2 combustion (i.e. CO_2 and H_2O; only a residual contribution of possible WGS or reverse WGS reactions, taking place in any case at temperatures higher than ca. 453 K, was estimated from mass balance under the conditions employed; this was also confirmed by independent tests including CO_2 or H_2O as reactants) were detected in the course of the runs, in agreement with previous results on catalysts of this type [6,15,17,25]. On this basis, values of percentage conversion and selectivity in the CO-PROX process are defined as:

$$X_{O_2} = \frac{F_{O_2}^{in} - F_{O_2}^{out}}{F_{O_2}^{in}} \times 100, \qquad X_{CO} = \frac{F_{CO}^{in} - F_{CO}^{out}}{F_{CO}^{in}} \times 100,$$

$$S_{CO_2} = \frac{X_{CO}}{2.5 X_{O_2}} \times 100$$

where X and S are the percentage conversion and selectivity, respectively, and F is the (inlet or outlet) molar flow of the indicated gas.

Operando-DRIFTS analysis of the sample was carried out using a Bruker Equinox 55 FTIR spectrometer fitted with an MCT detector. The DRIFTS cell (Harrick) was fitted with CaF_2 windows and a heating cartridge that allowed samples to be heated to 773 K. Aliquots of ca. 100 mg were calcined in situ (in a similar way as employed for the catalytic tests) and then cooled to 298 K under diluted oxygen before introducing the reaction mixture and heating in a stepped way, recording one spectrum (average of 50 scans at $4\ cm^{-1}$ resolution) every 10 K after the signal of the paramagnetic analyser (coupled on-line for O_2 analysis at the outlet of the DRIFTS cell) becomes constant (i.e. steady conditions). The gas mixture (either for joint CO and H_2 oxidation—1% CO + 1.25% O_2 + 50% H_2 in Ar, or for individual CO or H_2 oxidation reactions—1% CO + 1.25% O_2 or 50% H_2 + 1.25% O_2, Ar balance in any case) was prepared using mass flow controllers with ca. $100\ cm^3\ min^{-1}$ passing through the catalyst bed at atmospheric pressure, which corresponds to conditions similar to those employed for the reaction tests with the tubular reactor.

X-ray photoelectron spectra (XPS) were recorded with a Leybold–Heraeus spectrometer equipped with an EA-200 hemispherical electron multichannel analyzer (from Specs) and