Catalysis Today 229 (2014) 104–113

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Preferential oxidation of CO in excess H_2 over CuO/CeO_2 catalysts: Performance as a function of the copper coverage and exposed face present in the CeO_2 support

M. Monte[a], D. Gamarra[a,1], A. López Cámara[a], S.B. Rasmussen[a,b,2], N. Gyorffy[c], Z. Schay[c], A. Martínez-Arias[a,*], J.C. Conesa[a,*]

[a] Instituto de Catálisis y Petroleoquímica, CSIC, Campus de Cantoblanco. c/ Marie Curie 2, 28049 Madrid, Spain
[b] Department of Chemistry, Technical University of Denmark, Kemitorvet 207, 2800 Kgs. Lyngby, Denmark
[c] Institute of Isotopes, Hungarian Academy of Sciences, H 1525 Budapest, Hungary

ARTICLE INFO

Article history:
Received 30 June 2013
Received in revised form 11 October 2013
Accepted 13 October 2013
Available online 2 December 2013

Keywords:
Nanostructured CuO/CeO_2 catalysts
CO-PROX
Operando-DRIFTS
EPR
TPR
DFT

ABSTRACT

CuO/CeO_2 catalysts where the support has different nanoparticle shapes exposing different lattice planes are examined for the preferential oxidation of CO in the presence of excess H_2 (CO-PROX reaction) in *operando* DRIFTS conditions. Even for catalysts with same surface concentration of Cu the selectivity for CO_2 formation is found close to 100% up to higher temperatures when the support is in form of nanocubes (exposing the less stable (0 0 1) lattice planes). DRIFTS data allow relating this to a higher stability of the Cu species forming the Cu^+ carbonyls associated to the high activity and selectivity, so that they are fully reduced at higher temperature in agreement with TPR data. DFT calculations show that CuO nanoparticles interact more strongly (distorting more their structure) with the CeO_2 (0 0 1) surface than with the (1 1 1) surface, while XRD indicates that the formation of well developed CuO nanocrystals is more difficult on nanocube shaped CeO_2 than on other CeO_2 morphologies. Also EPR spectra show that the CuO entities nucleate on the ceria nanocubes differently. The higher stabilization of the oxidized state indicated by DFT, together with the mentioned structural distortion, may be then the reason for the improved selectivity.

1. Introduction

Hydrogen production from hydrocarbons for its use in proton exchange membrane fuel cells requires a final purification step to decrease the CO concentration resulting after reforming and water-gas shift (WGS) steps. Preferential or selective catalytic oxidation of CO by O_2 in the H_2-rich stream (CO-PROX) is considered as most interesting from practical and economical points of view, most particularly for mobile applications [1]. Among different possible alternatives, catalysts combining copper and cerium oxides have demonstrated promising characteristics for CO-PROX while they are able to compete with less economically interesting noble metal catalysts [1,2].

Main properties of $CuO–CeO_2$ systems for this process appear related to synergetic interactions between the two constituent oxides which determine interfacial characteristics [3]. This is based on the fact that active sites for the CO oxidation reaction, whose relative activity with respect to that of competing H_2 oxidation reaction basically determines overall performance for the process [4–6], are proposed to be located at such interface between both oxides [4,5,7,8], being formed by Cu^+ entities which result from ceria-promoted reduction of dispersed CuO upon interaction with the reactant mixture [4,5,9–14]. In turn, active sites for the H_2 oxidation reaction are apparently formed over the dispersed copper oxide particles upon extension of their reduction from the interface [5]. The fact that different active sites could be responsible for the two competing reactions is in agreement with kinetic measurements showing the absence of dependence of CO and H_2 oxidation rates with respect to H_2 and CO partial pressures, respectively, thus suggesting no important competency between the two reactants for the active sites [6,15]. However, it cannot be discarded that some degree of competency arises at high reaction temperature, in the non-selective region, when CO desorption from active reduced copper sites becomes favoured, even though, to the best of our knowledge, no direct evidence for this is available yet [16]. Indeed, kinetic models are available in which such competency appears also reflected [17]; certainly, the origin of the discrepancy in macroscopic kinetic results can be related to the continuous changes in surface chemical characteristics upon interaction with the reactant mixture as a function of reaction temperature, nature of reactant

---

[*] Corresponding authors. Tel.: +34 5915854940; fax: +34 5915854766.
E-mail addresses: amartinez@icp.csic.es (A. Martínez-Arias), jcconesa@icp.csic.es (J.C. Conesa).

[1] Present address: Universidad de Extremadura, Campus de Badajoz, Avda. Elvas s/n. Edificio Guadiana, 06006 Badajoz, Spain.

[2] Present address: Haldor Topsøe A/S, Nymøllevej 55, 2800 Kgs. Lyngby, Denmark.

0920-5861/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cattod.2013.10.078

mixture and type of sample examined [4,5,18,19]. Notwithstanding such controversy, there is general agreement that the mentioned copper oxide reduction process (related to an induction step taking place upon interaction of the catalyst with the reactant mixture [4,12]) leading to generation of active sites for the two reactions, as well as the catalytic activity over these sites, must in principle depend strongly on interfacial properties, which should be taken into account in order to explain observed ceria promoting effects [5,7,8,10,20].

A way to tune interfacial interactions between the two oxide components could consist in changing the geometric type of interacting surfaces. In this sense Skårman et al. reported a study on systems of copper oxide deposited on CeO_2 thin films prepared by rf magnetron sputtering showing the higher magnitude of synergetic effects between copper oxide and ceria (0 0 1) surfaces, compared to thermodynamically most stable (1 1 1) ones, for CO oxidation [21]. In a similar sense, Zhou et al. reported a higher CO oxidation activity of copper oxide dispersed on high-energy, more reactive (0 0 1) and (1 1 0) planes of CeO_2 nanorods prepared by a hydrothermal method in comparison with an analogous sample in which the ceria support was prepared by simple precipitation and which is assumed to expose mainly (1 1 1) surfaces [22]; in the same sense, NO reduction by CO was shown to be most favoured for CuO entities in contact with ceria nanorods compared with nanocubes or nanopolyhedra [23].

Concerning the CO-PROX application, in contrast to the two works just mentioned [21,22] CO oxidation was found to be most favoured over copper oxide deposited on ceria nanooctahedra (exposing (1 1 1) faces), these samples apparently displaying higher surface copper content, according to XPS measurements, than similar ones using as support ceria nanorods (exposing (1 1 0) and (0 0 1) faces) or nanocubes (exposing (0 0 1) faces) [24]. Our laboratory examined also recently this process over samples with the same wt.% loading of copper oxide (1 wt.%) supported on ceria with different surface morphologies (nanospheres, nanorods and nanocubes) [25]; it was shown there that the sample supported on ceria nanocubes displays an enhanced CO_2 selectivity during the process, which is attributed to the ability of such sample to keep a lower reduction level under reaction conditions; samples of Cu supported on nanorods or nanospheres, in contrast, displayed relatively similar reactivity behaviour, with activity and selectivity characteristics distinctly different from those displayed by ceria nanocube-based ones. However, it was not possible to discern whether such beneficial property could be related to the relatively larger size of interacting dispersed copper oxide particles achievable, as a consequence of its lower specific surface area, in such sample or to effects of interaction with the (0 0 1) face present in the nanocube-shaped ceria support [25], or both.

Within this context and in order to shed some more light on these issues, the present work analyses CO-PROX performance of catalysts of copper oxide deposited on different nanocrystalline ceria supports (nanorods and nanocubes). In this case, and taking into account differences in the specific surface area of the two ceria supports [25], besides catalysts with the same copper loading (1 wt.%) catalysts with the same nominal surface copper coverage have been also comparatively explored. For such purpose, characterization employing different techniques along with analysis of catalytic properties of the systems done by *operando*-DRIFTS has been performed in the present work. The results show that the improved CO-PROX selectivity appearing on the ceria nanocubes-supported sample, which was previously detected on 1 wt.% catalysts [25], is observed as well if samples with the same surface copper coverage are compared. The study is complemented with data from DFT calculations at the GGA+U level. These latter results, which are part of a more complete modelling study on this system to be published separately, suggest that interfacial interaction between CuO and the CeO_2 surface is stronger, so that the CuO structure is significantly distorted, when the ceria exposes the (0 0 1) crystal plane (dominant in the nanocube shape). This may explain the different reactivity and the higher resistance to reduction of copper (under CO-PROX conditions) to the state responsible for the H_2 molecule activation and the selectivity loss.

2. Experimental

2.1. Sample preparation

Procedures available in the literature have been employed to prepare CeO_2 supports in the form of nanorods and nanocubes [26]. For this, $Ce(NO_3)_3\ 6H_2O$ (Aldrich) used as the cerium precursor was dissolved along with NaOH in deionized water. Then, the mixture was introduced in Teflon flasks of 125 mL filled at 75% of the total volume and, after stirring, was held in a stainless steel autoclave and subjected to hydrothermal treatment during 24 h at 100 °C or 180 °C for the synthesis of ceria nanorods or nanocubes, respectively. After the hydrothermal treatment, the precipitates were separated by centrifugation, washed with deionized water and ethanol several times, followed by drying at 60 °C under air overnight. Then, the supports were calcined under air for 2 h at 500 °C. Specific surface area values for the supports (S_{BET}), based on analysis of nitrogen adsorption isotherms, were reported in a previous work, being 76 and 20 $m^2\,g^{-1}$ for CeO_2 nanorods and nanocubes, respectively [25].

Samples of copper supported on the two CeO_2 supports were prepared by incipient wetness impregnation of the supports with copper nitrate aqueous solutions. As mentioned above, besides two samples with 1 wt.% copper on the two supports (which imply surface Cu concentrations of 4.75 and 1.25 Cu atoms/nm^2 for the samples on NC and NR supports respectively, taking into account the S_{BET} values of the supports), samples with 0.59 and 0.16 wt.% copper (corresponding to average surface coverages of 0.74 and 0.75 Cu atoms/nm^2) were prepared on CeO_2 nanorods and nanocubes, respectively; these coverages are therefore equivalent to the value (0.73 Cu atoms/nm^2) of the sample prepared on CeO_2 nanospheres and containing 1 wt.% copper described in previous reports [4,25]. Following impregnation, the samples were dried overnight at 100 °C and finally calcined under air at 500 °C for 2 h. The samples will be called hereafter as 1Cu/CeO_2-NR, 1Cu/CeO_2-NC, 0.59Cu/CeO_2-NR and 0.16Cu/CeO_2-NC, the first number reflecting the Cu wt.% and the suffix the support morphology (NR and NC for nanorods and nanocubes, respectively).

2.2. Experimental techniques

Powder XRD patterns of the samples were recorded on a Seifert XRD 3000P diffractometer using nickel-filtered Cu K_α radiation operating at 40 kV and 40 mA, using a 0.02° step size and 2 s counting time per point. Analysis of the diffraction peaks was done with the computer program ANALYZE Rayflex Version 2.293.

For the EPR measurements, a Bruker EMX spectrometer with a 12 kW 10 in. magnet was employed. Samples (0.010–0.050 g) were placed into a micro-reactor cell made of quartz of spectroscopic purity, especially designed for pre-treatment of samples prior to EPR measurements, such that no transfer or other handling of sample was necessary between the calcination step and the acquisition of spectra at 77 K. After treatment at above 350 °C in a flow of 20–50 mL min^{-1} under 10% O_2/He the sample was cooled to room temperature in the oxygen containing gas. Thereafter, weakly adsorbed oxygen was removed by subjecting the sample to a mild vacuum, around 2×10^{-5} mbar, and the sample was cooled to 77 K in a liquid nitrogen-filled finger dewar. Low temperature spectra