

Inverse CeO₂/CuO Catalyst As an Alternative to Classical Direct Configurations for Preferential Oxidation of CO in Hydrogen-Rich Stream

A. Hornés,[†] A. B. Hungría,[‡] P. Bera,[†] A. López Cámara,[†] M. Fernández-García,[†]
A. Martínez-Arias,^{*,†} L. Barrio,[§] M. Estrella,[§] G. Zhou,[§] J. J. Fonseca,[§] J. C. Hanson,[§] and
J. A. Rodríguez[§]

*Instituto de Catálisis y Petroleoquímica, CSIC, C/ Marie Curie 2, Campus de Cantoblanco, 28049 Madrid, Spain,
Universidad de Cádiz, Departamento de Ciencia de Materiales, Ingeniería Metalúrgica y Química Inorgánica,
Facultad de Ciencias, 11510 Puerto Real, Cádiz, Spain, and Chemistry Department,
Brookhaven National Laboratory, Upton, New York 11973*

Received October 21, 2009; E-mail: amartinez@icp.csic.es

Production of H₂ for polymer fuel cells (PEMFC) is usually accomplished by a multistep procedure which includes catalytic reforming of hydrocarbons followed by water gas-shift (WGS) processes.^{1,2} However, due to the limited activities of current WGS catalysts, approximately 0.5–1.0 vol % of unconverted CO still remains in the effluent and needs to be decreased to a trace level to avoid poisoning of the Pt-based PEMFC anode. Preferential oxidation of CO (CO-PROX) upon external introduction of a small amount of oxygen in the H₂-rich stream resulting from reforming-WGS processes has been recognized as one of the most straightforward and cost-effective methods to achieve acceptable CO concentrations (below ca. 100 ppm).³ Supported noble metal catalysts, in particular those containing platinum or gold,^{3–5} have shown their ability for the process, and commercial systems based on supported platinum are available.⁶

Catalysts based on combinations between copper and cerium oxides constitute a more interesting alternative from an economical point of view and have also shown promising properties for the process.^{5,7,8} It is generally agreed that optimum catalytic properties for CO oxidation over copper-ceria catalysts are achieved in the presence of well dispersed copper oxide patches over ceria nanoparticles.^{7,9} This has been recently rationalized by spectroscopic analysis under reaction conditions of catalysts of this type showing that active sites for such a reaction, under CO-PROX conditions, are related to interfacial copper oxide entities which become partially reduced during the course of interaction with the reactant mixture, for which process ceria apparently plays an important promoter role.⁸ In turn, the mentioned study has shown that H₂ oxidation, the main reaction competing for the available oxygen with the CO oxidation one over this type of catalyst (their respective relative activity therefore determining the width of the practical conversion window, i.e. temperature range at which values close to 100% CO conversion with the lowest possible H₂ oxidation activity becomes achieved), is apparently promoted when the reduction of the copper oxide particles becomes extended to noninterfacial sites, suggesting that the performance for such a reaction can strongly depend on morphological characteristics of the copper oxide particles themselves.⁸ Such results, suggesting a possible separation (at least to a certain extent; it must be noted that both oxidation processes cannot most likely be treated as fully independent)^{7,10} between most active sites for the two main oxidation reactions (of CO and H₂, respectively) taking place along the CO-PROX process, obviously provide a key to modulation of the overall CO-PROX behavior of this kind of system.⁸ In this context, enhanced catalytic properties can be achieved by using,

instead of traditional direct catalyst configurations, in which copper oxide is dispersed onto ceria, inverse configurations in which large size copper oxide particles act as the support for ceria. The hypothesis proposes shifting hydrogen oxidation conversion to a higher temperature based on the fact that the reducibility of copper oxide particles with hydrogen is expected to decrease with increasing particle size,^{9,11} and considering that this type of catalyst operates under redox Mars-van Krevelen type mechanisms.¹² In turn, it is expected that the amount and properties of copper-ceria interfacial sites could be maintained in the inverse system to keep a high level of CO oxidation activity in the system.⁸

The inverse system has been synthesized by a microemulsion method, as detailed in Supporting Information. X-ray diffraction shows that the catalyst is constituted by CuO and CeO₂ with average crystal sizes of 21.8 and 5.3 nm, respectively (Supporting Information). The inverse configuration of the catalyst has been demonstrated by means of STEM-XEDS and HRTEM analyses (Supporting Information). As illustrated by Figure 1, the sample shows the presence of large CuO particles onto which small (about 5 nm) CeO₂ particles appear supported.

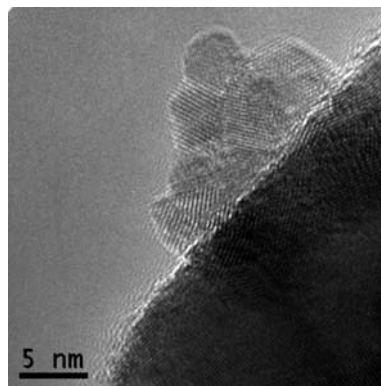


Figure 1. HRTEM image of the catalyst showing several CeO₂ nanoparticles supported over a CuO particle.

CO conversion achieved under a CO-PROX mixture for the inverse catalyst favorably compares with that obtained over a classical reference catalyst which displayed the highest CO oxidation activity among this series in a previous study,⁷ Figure 2. The wider full CO conversion window and higher CO₂ selectivity achieved over the inverse catalyst are, in accordance with the proposed hypothesis, a consequence of its lower activity for the H₂ oxidation reaction. This must be related to the limited reducibility of larger size CuO particles present in this catalyst.^{8,9,11} This has been demonstrated by means of *operando*-XRD

[†] CSIC.

[‡] Universidad de Cádiz.

[§] Brookhaven National Laboratory.

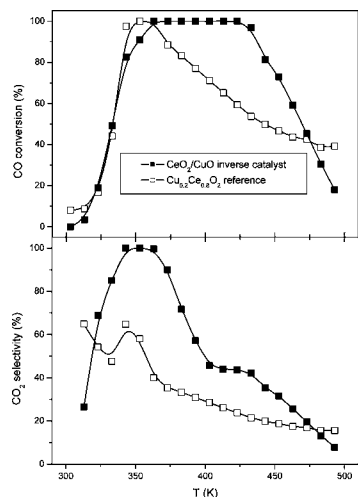


Figure 2. Catalytic activity under 1% CO, 1.25% O₂, and 50% H₂ (Ar balance) for the indicated catalysts. Top: CO conversion. Bottom: Selectivity to CO₂. Note CO₂ and H₂O are only products obtained from competing CO and H₂ oxidation reactions, respectively.

and -XAFS. XRD measurements under CO-PROX conditions show that the starting CeO₂/CuO sample becomes reduced to CeO_{2-x}/Cu above 470 K, Figure 3. The reduction is direct, and only a minute amount of Cu₂O intermediate could be inferred; this behavior is characteristic of large CuO particles reduced under either H₂ or CO.^{13,14} Another interesting feature is the evolution with temperature of the CeO₂ lattice size. Below 470 K, the CeO₂ lattice evolves as expected for thermal expansion. However, simultaneously with CuO reduction above 470 K, an extensive lattice expansion is produced which is related to ceria reduction;¹⁵ i.e., concurrent ceria and CuO reduction is produced, proving the strong copper–ceria interaction in the sample, in agreement with previous results.⁸ This is corroborated by XAFS measurements under reaction conditions (Supporting Information). In

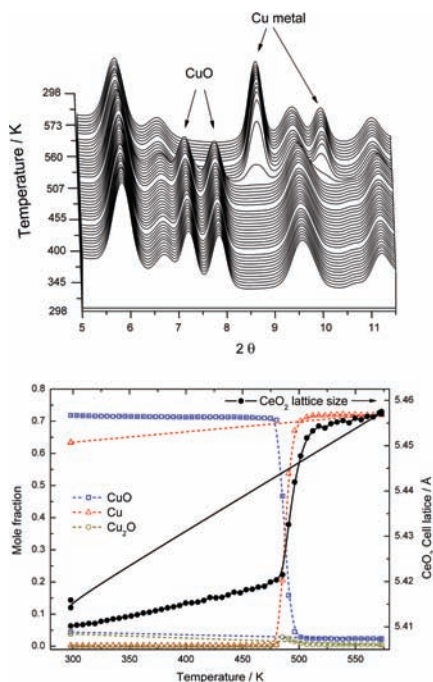


Figure 3. Top: Time resolved XRD patterns of the inverse catalyst taken under CO-PROX conditions. Bottom: Sequential Rietveld refinement of Cu species mole fractions and CeO₂ cell dimension.

contrast to the redox behavior of the inverse catalyst, the Cu_{0.2}Ce_{0.8}O₂ reference system was shown to become reduced at appreciably lower temperatures (ca. 400 K) under the same conditions and coinciding with the onset of H₂ oxidation.⁸ Sequential CuO → Cu₂O → Cu reduction was detected in that case, which must be due to the lower influence of kinetic effects during reduction of the highly dispersed very low size CuO particles present in the Cu_{0.2}Ce_{0.8}O₂ reference catalyst.^{7,8,13,16} Activity data collected during recording of XAFS spectra show that onset of H₂ oxidation takes place at ~425 K, before bulk reduction occurs (Supporting Information). This suggests that surface redox changes are mainly generating the active sites for that reaction; it must be considered the huge amount of bulk with respect to surface copper expected to be present in the large CuO particles in the inverse catalyst. In turn, previous studies have evidenced that active sites for the CO oxidation reaction are related to interfacial Cu⁺ species generated through a reductive process upon interaction with the CO-PROX reactant mixture.⁸ This has been explored by *operando*-DRIFTS which demonstrates the formation of such Cu⁺ states already upon contact with the reactant mixture at 303 K (Supporting Information). Redox/catalytic correlations provide evidence for the involvement of these active species on CO oxidation for the inverse CeO₂/CuO catalyst, in agreement with our recent investigation.¹⁷

Acknowledgment. A.H. and A.L.C. thank the MICINN and CSIC for FPU and JAE grants, respectively. P.B. thanks the sixth EC Framework Programme for a Marie Curie International Incoming Fellowship. Financial support by Comunidad de Madrid (ENERCAM S-0505/ENE/000304) and MICINN (CTQ2006-15600/BQU and CTQ2009-14527/BQU) is acknowledged. The work at BNL was financed by the U.S. Department of Energy (DE-AC02-98CH10086). L.B. acknowledges funding by the FP7 People program under the project Marie Curie IOF-219674.

Supporting Information Available: Experimental procedure; XRD and STEM-XEDS structural analysis, *operando*-XRD, -XAFS, and -DRIFTS analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Rostrup-Nielsen, J. R.; Sehested, J.; Nørskov, J. K. *Adv. Catal.* **2002**, *47*, 65.
- (2) Fu, Q.; Saltsburg, H.; Flytzani-Stephanopoulos, M. *Science* **2003**, *301*, 935.
- (3) Ko, E.-Y.; Park, E. D.; Lee, H. C.; Lee, D.; Kim, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 734.
- (4) Guzman, J.; Carrettin, S.; Corma, A. *J. Am. Chem. Soc.* **2005**, *127*, 3286.
- (5) Avgouropoulos, G.; Ioannides, T.; Papadopolou, Ch.; Batista, J.; Hocevar, S.; Matralis, H. K. *Catal. Today* **2002**, *75*, 157.
- (6) Farrauto, R.; Hwang, S.; Shore, L.; Ruettinger, W.; Lampert, J.; Giroux, T.; Liu, Y.; Ilinich, O. *Annu. Rev. Mater. Res.* **2003**, *33*, 1.
- (7) Gamarra, D.; Munuera, G.; Hungria, A. B.; Fernández-García, M.; Conesa, J. C.; Midgley, P. A.; Wang, X. Q.; Hanson, J. C.; Rodríguez, J. A.; Martínez-Arias, A. *J. Phys. Chem. C* **2007**, *111*, 11026.
- (8) Gamarra, D.; Belver, C.; Fernández-García, M.; Martínez-Arias, A. *J. Am. Chem. Soc.* **2007**, *129*, 12064.
- (9) Liu, W.; Flytzani-Stephanopoulos, M. *Chem. Eng. J.* **1996**, *64*, 283.
- (10) Martínez-Arias, A.; Hungria, A. B.; Munuera, G.; Gamarra, D. *Appl. Catal., B* **2006**, *65*, 207.
- (11) Luo, M.; Ma, J.; Lu, J.; Song, Y.; Wang, Y. *J. Catal.* **2007**, *246*, 52.
- (12) Martínez-Arias, A.; Gamarra, D.; Fernández-García, M.; Hornés, A.; Belver, C. *Top. Catal.* **2009**, *52*, 1425.
- (13) Kim, J. Y.; Rodríguez, J. A.; Hanson, J. C.; Frenkel, A. I.; Lee, P. L. *J. Am. Chem. Soc.* **2003**, *125*, 10684.
- (14) Wang, X.; Hanson, J. C.; Frenkel, A. I.; Kim, J. Y.; Rodríguez, J. A. *J. Phys. Chem. B* **2004**, *108*, 13667.
- (15) Martínez-Arias, A.; Gamarra, D.; Fernández-García, M.; Wang, X. Q.; Hanson, J. C.; Rodríguez, J. A. *J. Catal.* **2006**, *240*, 1.
- (16) Pike, J.; Chan, S.-W.; Zhang, F.; Wang, X.; Hanson, J. *Appl. Catal., A* **2006**, *303*, 273.
- (17) Bera, P.; Hornés, A.; López Cámara, A.; Martínez-Arias, A. *Catal. Today* (in press, d.o.i.:10.1016/j.cattod.2009.08.010).

JA9089846