Journal of Catalysis 263 (2009) 189–195

Contents lists available at ScienceDirect

Journal of Catalysis

www.elsevier.com/locate/jcat

Preferential oxidation of CO in rich H_2 over CuO/CeO_2: *Operando*-DRIFTS analysis of deactivating effect of CO_2 and H_2O

Daniel Gamarra, Arturo Martínez-Arias *

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

ARTICLE INFO

Article history:
Received 14 November 2008
Revised 16 January 2009
Accepted 12 February 2009
Available online 24 February 2009

Keywords:
$CuO–CeO_2$ catalysts
CO-PROX
Operando-DRIFTS
CO_2
H_2O
Deactivation

ABSTRACT

A catalyst of copper oxide supported on nanostructured ceria has been examined with the aim of exploring deactivating effects produced by CO_2 or H_2O presence on its activity for preferential oxidation of CO in a H_2-rich stream. For this purpose, the catalyst is explored by means of *operando*-DRIFTS experiments. The results allow determining most relevant deactivating effects induced by CO_2 and H_2O. These are mainly related to modifications of interfacial sites upon formation of specific carbonates and a blocking effect induced by the presence of adsorbed molecular water, respectively, which limit redox/catalytic activity of the interfacial zone of the catalyst active for CO oxidation. Such modifications are directly evidenced by the difficulties of ceria to promote the generation of partially reduced states at interfacial sites of the dispersed copper oxide particles or to propagate the reduction over such particles, which affects to the hydrogen oxidation activity of the catalyst, leading on the whole to a general decrease of the CO-PROX performance of the system.

1. Introduction

Production of H_2 for polymer fuel cells (PEMFC) is usually accomplished by a multi-step process that includes catalytic reforming of hydrocarbons or oxygenated hydrocarbons followed by water–gas shift (WGS) [1,2]. The gas stream obtained after these processes presents in most cases 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 in the H_2-rich stream resulting from such processes (CO-PROX) has been recognised as one of the most straightforward and cost-effective methods to achieve acceptable CO concentrations (below ca. 100 ppm), particularly when dealing with small size stationary units or on-board H_2 production [3–8].

Catalysts based on closely interacting copper oxide and ceria have exhibited promising properties in terms of activity and selectivity, while their lower cost with respect to formulations based on noble metals could make them strongly competitive [3,4,6,7,9–16]. The particular ability of this class of catalysts for the CO-PROX or related processes has been essentially attributed to the synergistic redox properties produced upon formation of copper oxide–ceria interfacial sites [4,6,10,11,17–27]. In this sense, generally speaking, the properties of copper oxide entities for CO oxidation promotion apparently depend strongly on their dispersion degree and/or associated degree of interaction with ceria [11,17,18,28]. Reaction models for CO oxidation (competing or not with H_2 oxidation, as it occurs under CO-PROX conditions) have been proposed on the basis of indirect analysis of redox or catalytic properties for this type of catalysts [29,30], while direct evidence on redox changes taking place in the catalyst under the reactant atmosphere, providing details on the nature of active sites for the processes taking place under CO-PROX conditions in this type of catalysts, has been recently reported on the basis of *operando* spectroscopic studies [11,31,32]. This has allowed establishing redox–catalytic correlations in oxidised copper–ceria catalysts, which are basically shown to involve ceria promoting effects on the partial reduction of interfacial dispersed CuO entities, apparently constituting active sites for CO oxidation; in turn, a separate process of extended reduction of such entities can apparently provide sites active for H_2 oxidation [32].

Nevertheless, such analyses have been typically performed upon employing simple CO-PROX reactant mixtures without including gases like CO_2 and/or H_2O also present in the reforming-WGS stream [3]. In this respect, catalytic tests have demonstrated deactivating effects of both molecules on the CO-PROX performance of $CuO–CeO_2$ catalysts [3,12,28,33,34]. On the basis of such catalytic results, Mariño et al. proposed that gradual CO oxidation activity and CO_2 selectivity decrease with increasing CO_2 content in the stream up to 15% could be related to competitive adsorption of CO_2 on the active copper sites and/or inhibition of oxygen mobility upon formation of carbonates on the ceria support [12]. In turn, Avgouropoulos et al. observed that the deactivating effect induced

---

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

0021-9517/$ – see front matter
doi:10.1016/j.jcat.2009.02.012

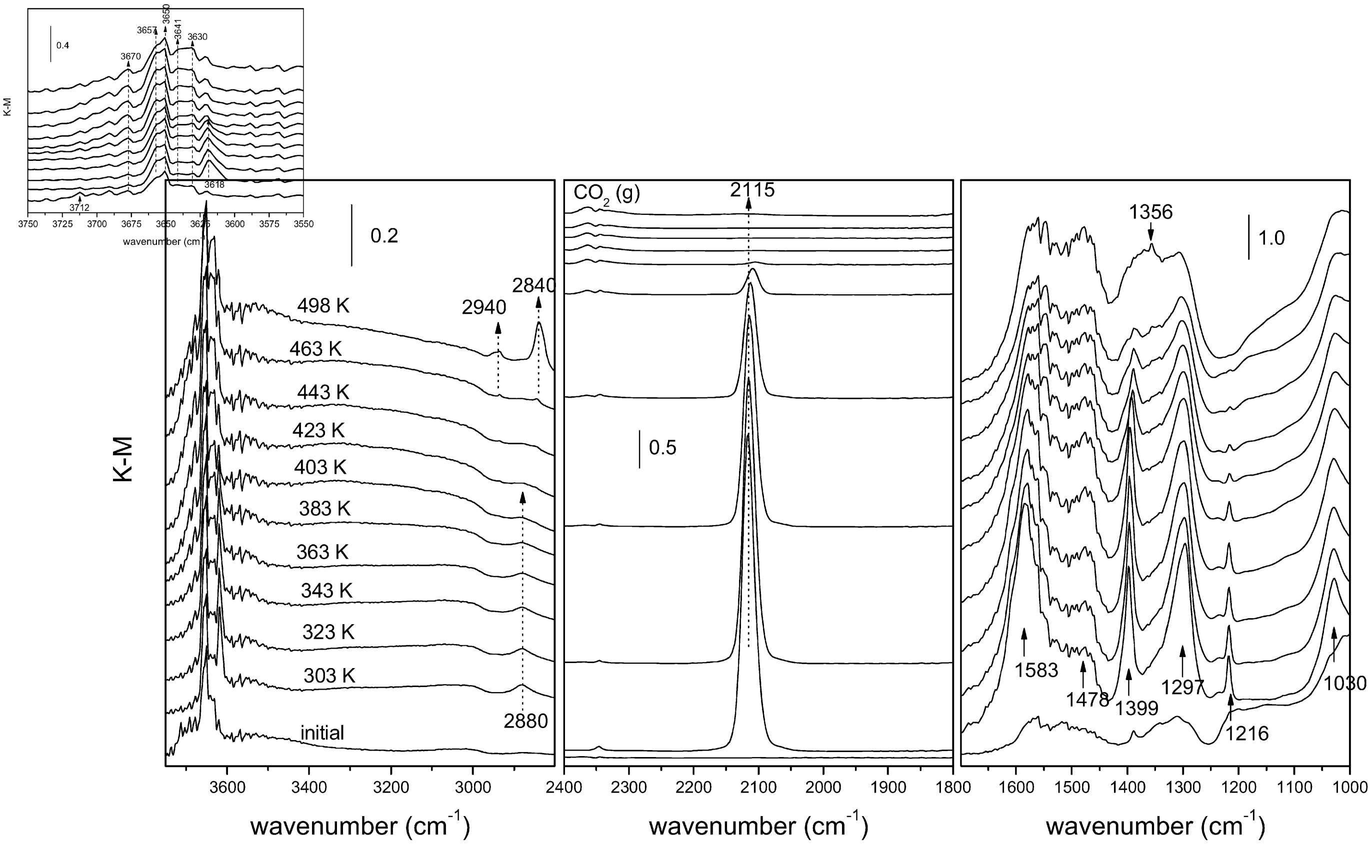

Fig. 1. DRIFTS spectra of CuO/CeO_2 recorded under the simple $CO + H_2 + O_2$ CO-PROX mixture. As indicated in the left part, the bottom spectrum corresponds to the initial one prior to introduction of the reactant mixture; the rest corresponds to spectra recorded every 20 K from 303 to 463 K, from bottom to top, except for the top one which was recorded at 498 K. The top left inset expands the zone corresponding mainly to hydroxyl species.

by 15% CO_2 apparently became more intense with the increase of copper content in $CuO–CeO_2$ catalysts prepared by hydrothermal method while additional 10% water present in the feed suggested water as a stronger CO oxidation inhibitor than CO_2 [28,34]. Park et al. proposed in their analysis of $CuO–CeO_2/Al_2O_3$ CO-PROX catalysts, on the basis of catalytic activity/stability tests and CO_2/H_2O TPD studies, that the main cause for the decrease in catalytic activity with CO_2 and H_2O in the feed is related to competitive CO and CO_2 adsorption as well as blockage of active sites by water at low reaction temperature [33]. Nevertheless, direct under working conditions examination of such deactivating effects has not, to the best of our knowledge, been reported. The present work aims to get details on such deactivating effects by using DRIFTS spectroscopy under reaction conditions with on line MS gas analysis.

2. Experimental

A sample of copper oxide supported on CeO_2 (Cu wt% of 1.0) was prepared by incipient wetness impregnation of a nanostructured CeO_2 support prepared by microemulsion (in a similar manner as described above) with copper nitrate aqueous solutions. Following impregnation, the sample was dried overnight at 373 K and finally calcined under air at 773 K for 2 h to yield a sample with $S_{BET} = 107\ m^2\,g^{-1}$. Characterisation details for both the support employed and the final catalyst are available elsewhere [21, 31,35].

DRIFTS spectra were 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 under diluted oxygen at 773 K and then cooled to 298 K under the same atmosphere followed by extensive purging under inert gas at room temperature before introducing the reaction mixture and heating in a stepped way, recording one spectrum (average of 25 scans at 4 cm^{-1} resolution) typically every 20 K after the signal of the different monitored gases (analysed on line by means of a quadrupole mass spectrometer Pfeiffer Omnistar) becomes constant at every reaction temperature (i.e. steady conditions). Gas mixtures (a simple reference one with 1% CO + 1.25% O_2 + 50% H_2 in He and two other having additionally either 15% CO_2 or 10% H_2O) were prepared using mass flow controllers and a perfusion syringe with ca. 100 $cm^3\,min^{-1}$ passing through the catalyst bed at atmospheric pressure. Analysis of the spectra has been carried out by using OriginPro 7 SR4 software.

3. Results and discussion

DRIFTS experiments recorded under simple $CO + H_2 + O_2$ CO-PROX mixture are displayed in Fig. 1. Changes produced upon contact with the reactant mixture are observed in three distinct spectral zones. The first zone at higher wavenumber displays bands corresponding mainly to hydroxyl species. These include, on the basis of previous analyses of ceria-related materials, isolated hydroxyls giving rise to relatively narrow bands at ca. 3712–3690 cm^{-1} (mono-coordinated to surface cerium cations), as well as a series of bands or shoulders in the 3670–3629 cm^{-1} range (attributable to bi- or tri-coordinated species bonded on more or less unsaturated cerium cations); additionally, associated species giving a broad band extending from ca. 3800 to 3000 cm^{-1} are detected [36,37].

A second spectral zone below 1700 cm^{-1} exhibits bands due to carbonate or related species, basically chemisorbed on ceria [37–

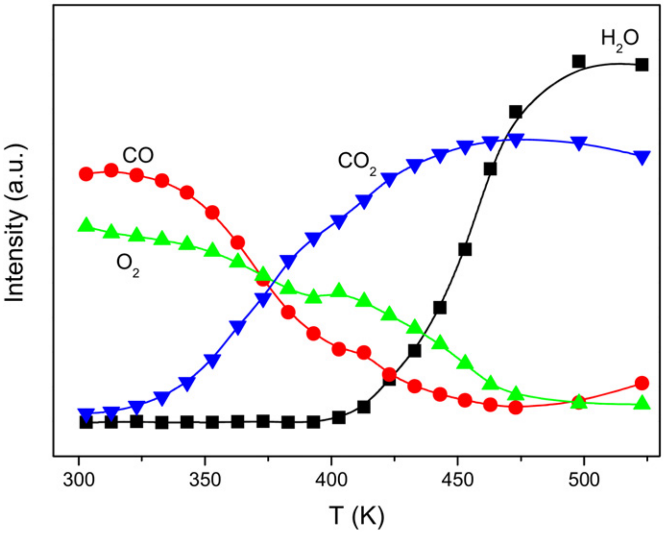

Fig. 2. MS evolution of the indicated gases during the run performed under the simple CO-PROX CO–H_2–O_2 mixture performed with the DRIFTS cell (corresponding to spectra presented in Fig. 1). Adequate corrections for CO_2 contributions to $m/e = 28$ signal have been made in order to quantify CO, according to previous calibration measurements.

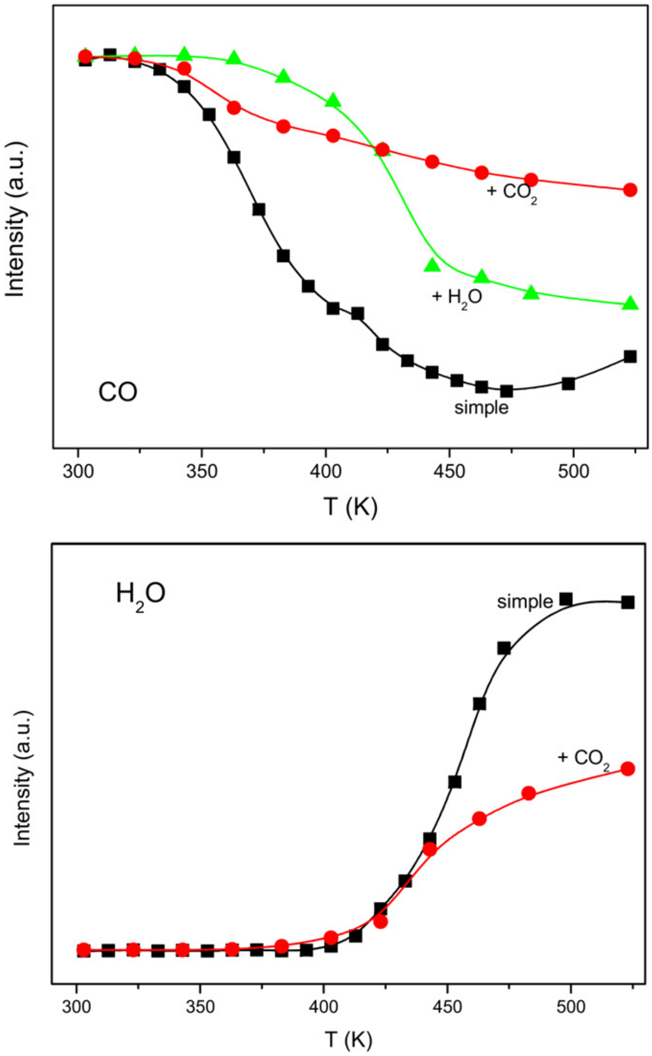

Fig. 3. MS evolution of CO (top) and H_2O (bottom) during CO-PROX runs performed with the DRIFTS cell under simple ($CO + H_2 + O_2$) reactant mixture or mixtures additionally containing either CO_2 or H_2O (note, in this latter experiment, H_2O evolution could not be determined neither directly nor indirectly, due to the relatively high H_2O and H_2 concentrations employed).

40]. Most intense peaks in this zone are ascribed to bidentate carbonates at ca. 1583 and 1297; a combination band at ca. 2880 cm^{-1} (see the highest wavenumber zone at the left of Fig. 1), particularly apparent in lower temperature spectra, is also attributed to these species. A band at ca. 1478 cm^{-1} may correspond to the antisymmetric stretching of the terminal CO bonds in poly- or mono-dentate carbonates (the corresponding symmetric mode would appear as an overlapped band at ca. 1350 cm^{-1}) [37]; nevertheless, it cannot be discarded that the band at ca. 1478 cm^{-1} may belong to a particular type of carbonite (CO_2^{2-}) species [41]. The band at 1216 cm^{-1}, along with that at 1399 cm^{-1} and a shoulder at ca. 1600 cm^{-1}, are attributed to hydrogen carbonate species [37,40]; this is confirmed by the presence of a sharp OH stretching vibration at ca. 3618 cm^{-1} also belonging to these species which must be formed upon interaction of CO (or CO_2) with monodentate hydroxyls (giving rise to a band at ca. 3712–3690 cm^{-1} in the spectrum of the original sample which disappears upon contact with the reactant mixture) [37,40]. In addition, the formation of formate species at temperatures above ca. 463 K is evidenced by bands at 2940 and 2840 cm^{-1}, related to C–H stretching mode or a combination band, while other intense features of these species correspond to symmetric and asymmetric ν_{OCO} modes which must yield bands at ca. 1330–1370 and 1550 cm^{-1} [39], apparently overlapped on bands due to other carbonate-type species.

The other spectral zone (at intermediate frequencies) shows the formation of CO_2(g), evolving in accordance with CO oxidation activity (*vide infra*), and a carbonyl species (a Cu^+-carbonyl giving rise to a band at ca. 2115 cm^{-1}, which apparently shifts gradually to the red down to ca. 2107 cm^{-1} with increasing temperature up to 383 K, practically disappearing above that temperature, most likely due to thermal stability effects [19]; note the assignment is in accordance with previous reports, in which details can be found to justify it [19,21,42]). The presence of these Cu^+-CO species already upon initial contact with the reactant mixture at 303 K is consistent with the easy (ceria-promoted) reduction of copper in the catalyst, considering that a fully oxidised state of copper is present in the initial calcined catalysts [31]. In this sense, it must be noted that room temperature reduction of copper in this catalyst upon interaction with CO has been previously demonstrated by EPR and XPS [19,21,31], while recent CO-TPR results on catalysts of this type evidence an important CO consumption at room temperature, most likely related to such low temperature reduction process [43].

Fig. 2 displays, as an example, the evolution of all the gases that have been monitored on line by mass spectrometry (MS), in this case corresponding to the DRIFTS experiments displayed in Fig. 1. In turn, Fig. 3 compares the effects of introducing either CO_2 or H_2O in the reactant mixture during experiments performed with the DRIFTS cell and for gases representative of CO and H_2 oxidation reactions. The results reveal differences in the respective deactivating effects as a function of reaction temperature. While CO_2 apparently induces a strong CO oxidation activity decrease during the whole temperature range, the deactivating effect of H_2O is particularly strong at temperatures below ca. 380 K, at which CO oxidation is strongly hindered, being relatively weaker above that temperature.

Explanations for these behaviours can be achieved upon comparative analysis of the DRIFTS spectra as a function of the specific CO-PROX reactant mixture employed. Fig. 4 displays the results obtained in the presence of CO_2 in the mixture. A first spectrum was taken under CO_2–H_2–O_2 mixture (i.e. prior to introducing CO in the feed). In this condition, the generation of various carbonate-type species was observed, mainly hydrogen carbonate (bands or

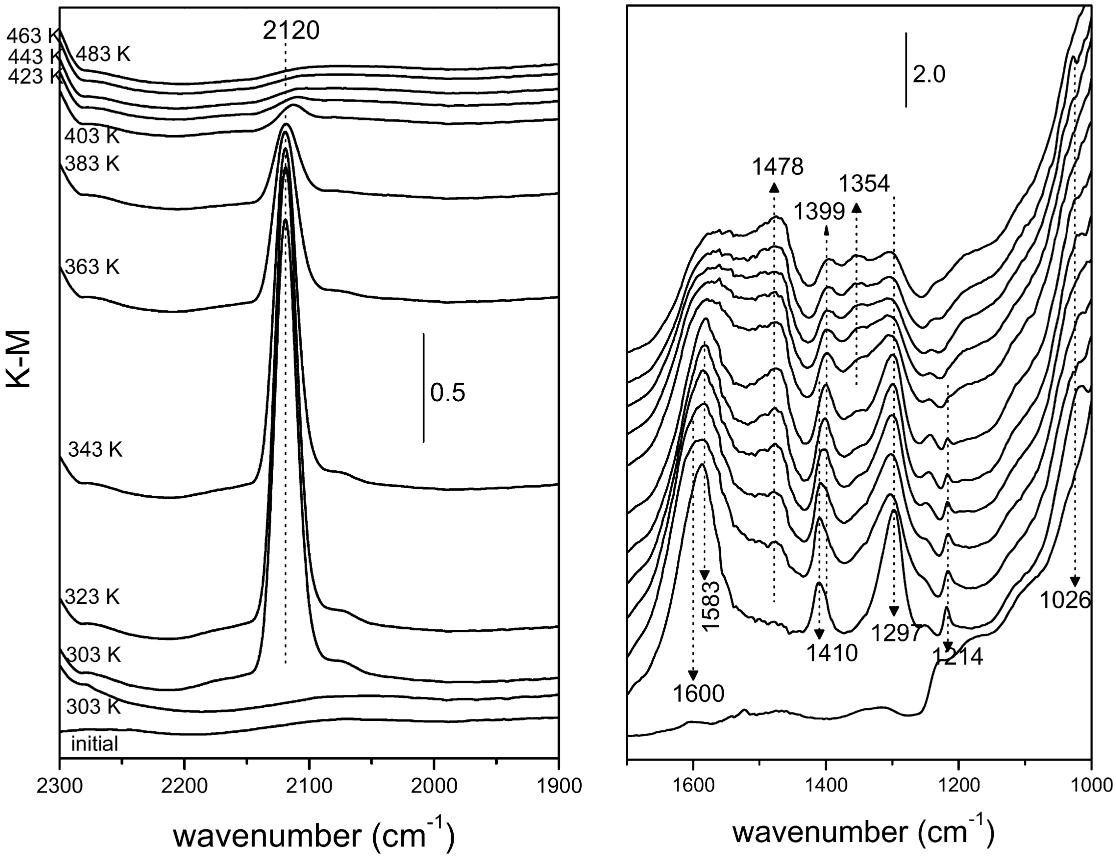

Fig. 4. DRIFTS spectra of CuO/CeO$_2$. The bottom one corresponds to the initial spectrum recorded prior to introduction of the gas mixture. The rest were recorded at the temperatures indicated in the left part (the same for those in the right part from bottom to top). Following calcination and recording of the initial spectrum, the one just above it was recorded under 1.25% O$_2$ + 50% H$_2$ + 15% CO$_2$ (i.e. with no CO in the mixture). The rest were recorded under CO–H$_2$–O$_2$–CO$_2$ CO-PROX mixture.

shoulders at 1214, 1399–1410 and ca. 1600 cm^{-1}) and bidentate carbonate (bands at ca. 1583 and 1297 cm^{-1}). Formation of this type of species in the absence of CO suggests that their formation is basically related to CO$_2$ interaction with the ceria surface of the catalyst; note in this sense that analogous species detected upon contact with the simple (without CO$_2$) CO-PROX mixture at 303 K (Fig. 1) could be related to CO$_2$ formed by CO oxidation (note a small but measurable activity is produced at that temperature) which could justify its formation from the very beginning in such case. Some small modification of such carbonate-type species is produced when CO is introduced in the mixture, according to the apparent broadening detected in the most intense bands appearing at ca. 1600 cm^{-1} (this could also tentatively explain an increase of a shoulder at ca. 1245 cm^{-1}, that could be related to some modification in the chemical environment of such species). Nevertheless, the main change induced by introduction of CO in the mixture in the carbonate region of the spectrum is related to the increase of a band at 1478 cm^{-1}, which, as mentioned above, could be related to carbonate (poly- or mono-dentate species, according to discussion elsewhere [37]; in such case, the corresponding symmetric stretching mode would correspond to the band at 1354 cm^{-1}, most apparent at higher reaction temperature) or carbonite species. In case such species corresponds to carbonate entities, it would most likely be formed upon CO$_2$ adsorption [37], and on ceria sites at the CuO–CeO$_2$ interface as a consequence of a CuO-promoted reductive process produced upon interaction with CO; evidences for occurrence of such ceria reduction at this relatively low temperature can be found elsewhere [21]. In contrast, carbonite species would most likely be formed upon CO interaction with reduced ceria [41], most probably at interfacial sites at which low temperature reduction would be CuO-promoted [21]. Along with formation of the band at 1478 cm^{-1} upon introduction of CO in the mixture, it is observed the appearance of the Cu$^+$ carbonyl at 2120 cm^{-1}, somewhat shifted to the blue with respect to the homologous spectra recorded in the absence of CO$_2$ in the reactant stream (Fig. 1). This suggests a lower influence of the copper–ceria interaction on the red shift of the Cu$^+$ carbonyl frequency in this case [19,21,42], taking into account comparison with corresponding stable species detected on pure Cu$_2$O [44]. This could be caused by the presence of the carbonate and/or carbonite species giving rise to the band at 1478 cm^{-1} in the environment of the Cu$^+$ adsorption sites, strongly predominant, as a difference with experiments performed under simple CO–H$_2$–O$_2$ mixture, in the presence of CO$_2$ in the feed, as will be examined in more detail in a separate contribution in the context of analysis of the CO oxidation reaction over catalysts of this type [45]. Besides this, other differences between spectra in the absence or presence of CO$_2$ in the reactant stream (Figs. 1 and 4) are related to the relatively higher intensity of carbonate-related species detected (as a rough estimation, the integrated intensity in the 1700–1000 cm^{-1} range is ca. 1.7 times higher in the presence of CO$_2$ when comparing spectra recorded at 303 K) and lower Cu$^+$ carbonyl intensity in the presence of CO$_2$ in the stream (Fig. 5). This latter was indeed shown in former contributions to be a fingerprint of CO oxidation activity in this type of catalysts [11,31,32], as it is also accomplished in this case according to comparison between Figs. 3 and 5 (note the Cu$^+$ carbonyl intensity decrease with increasing reaction temperature must basically reflect thermal stability effects [19]). On the basis of these results, the deactivating effect induced by CO$_2$ presence in the feed over CO oxidation activity must be mainly related to the hindering of interfacial redox activity induced by formation of carbonates and/or carbonites at interfacial ceria sites,

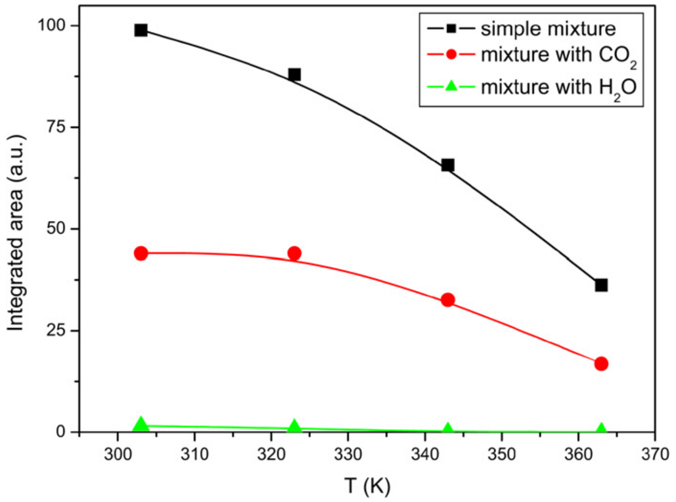

Fig. 5. Intensity of the Cu^+ carbonyl as a function of reaction temperature under the indicated CO-PROX mixtures. Overlapping CO(g) contributions were subtracted as required for this determination by using a reference run performed over inert KBr under the same experimental conditions.

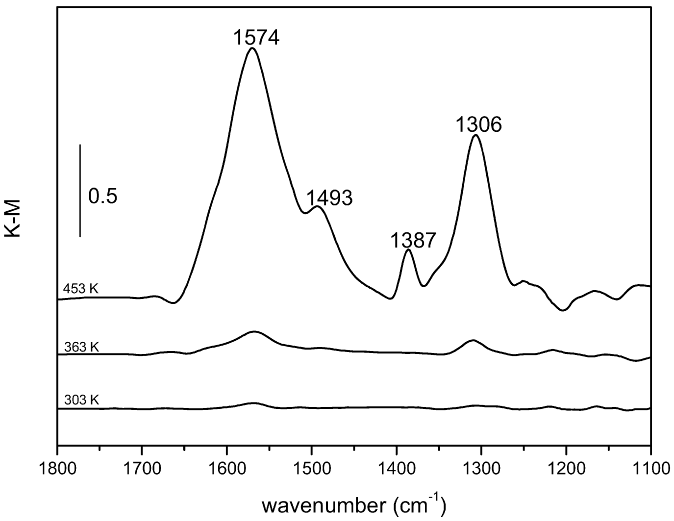

Fig. 6. DRIFTS spectra of the CeO_2 support recorded under the simple CO + H_2 + O_2 CO-PROX mixture at the indicated temperatures.

which limits the ceria-promoted reduction leading to generation of partially reduced CuO_x active sites at such interfaces, taking into account our previous hypothesis on the nature of active sites for this reaction [32]. Evidence for the interfacial location of the carbonate species formed can be based on differences with spectra recorded under CO-PROX conditions for the copper-free ceria support, Fig. 6, for which practically no oxidation activity was detected below ca. 453 K. Thus, while the carbonate-related species formed for copper-free ceria appear fairly similar to those detected for CuO/CeO_2 (basically bidentate species giving most intense bands at 1574 and 1306 cm^{-1} and poly- or mono-dentate ones at 1493 and 1387 cm^{-1}; note there is a certain shift in these values with respect to those observed for CuO/CeO_2, Fig. 1), they begin to appear at comparatively higher temperature in the absence of copper, thus revealing a promoting effect of copper oxide on its formation and its possible location at ceria positions at or close to the oxide–oxide interface (which could also explain the shift in bands positions).

On the other hand, the presence of CO_2 in the reactant mixture apparently has also an important detrimental influence on H_2 oxidation, according to Fig. 3. This can be related to a CO_2-induced impediment for propagation of the reduction (also promoted to some extent, smaller than the effect produced over interfacial sites, by ceria) over the dispersed CuO particles, which could provide most active sites for such reaction [32], as suggested by recent *operando*-XANES investigation on another catalyst of this type [46].

The low CO oxidation activity detected at low temperature in the presence of water in the feed (Fig. 3) is reflected by the strong hindering of formation of Cu^+ carbonyls (Figs. 5 and 7). The DRIFTS spectra evidence a strong hydroxylation degree for the surface of the sample under this condition (Fig. 7). This is evidenced by the strong intensity of a broad band at ca. 3317 cm^{-1}, which along with weaker ones at ca. 3692 and 1625 cm^{-1} can be attributed to the presence of undissociated water molecules on the sample surface (the two former correspond to OH stretching modes and the latter to HOH bending [37]). The significant decrease of these species at temperatures above ca. 373 K allows onset of CO oxidation (Fig. 3). Therefore, it appears that the reaction onset shift is mainly related to a water-induced blocking phenomenon which prevents access of the reactant molecules to the interfacial active sites for consequent reductive activation and reaction. Although above that temperature, the formation of hydroxyls at that active region could somewhat limit the interfacial redox processes and consequently the CO oxidation activity, the deactivation effect appears lower than that observed in the presence of CO_2 in the mixture (Fig. 3), thus indicating the greater hindering of interfacial redox activity induced by carbonate-type species.

The region of the spectra related to carbonate-type species reflects also the significant hydroxylation degree present over the sample, leading to frequency modifications for this type of species or formation of new type of complexes [38,39], as well as a general intensity decrease for this type of species (ca. half integral intensity in the 1700–1000 cm^{-1} range, comparing spectra at 303 K in the absence and presence of water in the feed). Thus, bands at 1554 and 1325 cm^{-1} may correspond to bidentate carbonates while above ca. 383 K bands are formed at ca. 1547 and 1372 cm^{-1}, which along with those at 2935 and 2845 cm^{-1} can correspond to formate species [39]; we do not believe this indicates onset of WGS at that temperature since, as mentioned above, WGS activity is residual below ca. 473 K in this type of catalysts and furthermore requires copper reduction to a metallic state [47], likely far from being achieved under the employed conditions according to XANES analysis of another catalyst of this type [46]. It cannot be fully discarded that the band detected at ca. 1345 cm^{-1} may correspond to the mentioned formate species too, although it shows a parallel evolution with a band at 1438 cm^{-1}, suggesting that it may correspond to mono- or poly-dentate carbonates (most intense terminal CO stretching modes) [37,38], somewhat shifted with respect to analogous bands detected in the absence of water in the feed as a consequence of the relatively higher hydroxylation degree of the sample surface. Other smaller contributions are detected at ca. 1510 and 1305 cm^{-1} which could be related to the formation of carboxylate species [38], while small amounts of hydrogen-carbonate species (bands or shoulders at ca. 1600 and 1399 cm^{-1}) can also be formed at relatively high temperature. It is noteworthy that, as it was observed in the presence of CO_2 (Fig. 4), onset of CO oxidation (above ca. 373 K) is accompanied by generation of the band at 1438 cm^{-1} (1478 cm^{-1}without water in the feed) suggesting, as outlined above, that formation of the corresponding carbonate (or carbonite, see above discussion) species can be associated to the interfacial reduction processes associated to generation of active sites for the reaction. Further experiments are in course in order to corroborate and get details on this type of correlation.

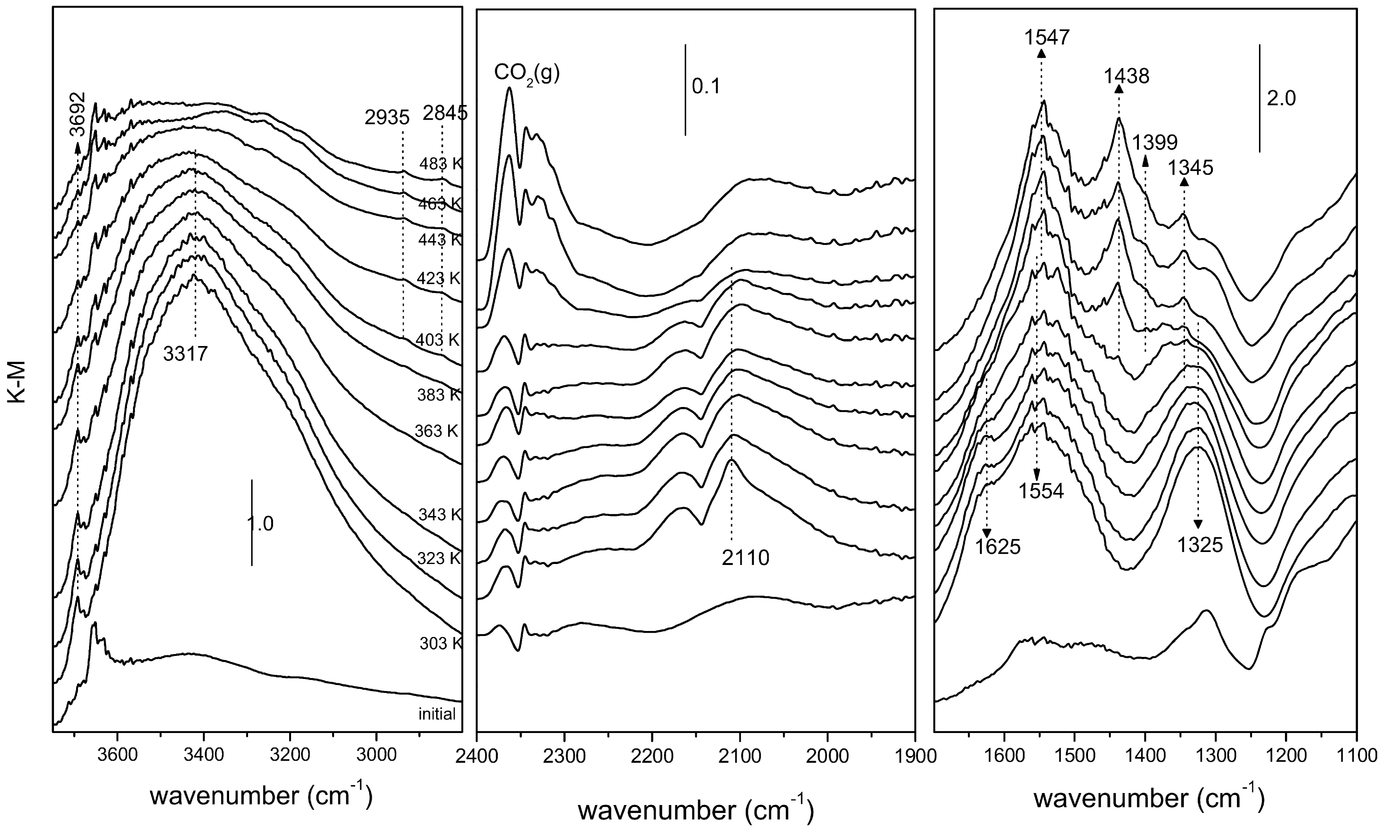

Fig. 7. DRIFTS spectra of CuO/CeO$_2$. The bottom one corresponds to the initial spectrum recorded prior to introduction of the gas mixture. The rest were recorded at the temperatures indicated in the left part (the same for those in the middle or right parts from bottom to top) under CO–H$_2$–O$_2$–H$_2$O CO-PROX mixture.

4. Conclusions

A CO-PROX ceria-supported copper oxide catalyst has been examined with respect to deactivating effects induced by the presence of CO$_2$ or H$_2$O in the reactant stream. On the basis of *operando*-DRIFTS examination, a hindering of formation of Cu$^+$-carbonyls, fingerprint of CO oxidation activity over this type of systems [32], is detected in the presence of any of the two molecules in the feed. This is related to a decrease of CuO–CeO$_2$ interfacial redox activity as a consequence of the formation of carbonates on interfacial ceria sites in the presence of CO$_2$ in the reactant stream, which brings as a consequence a limitation in the capability for redox promotion by ceria of the generation of partially reduced CuO$_x$ interfacial sites most active for CO oxidation; in turn, apparent decrease of H$_2$ oxidation activity in the presence of CO$_2$ in the feed can be related to limitations in the ceria promoting effects towards propagating the reduction over the dispersed CuO particles, taking into account previous hypothesis for the nature of active sites for such reaction [32]. On the other hand, the deactivating effect of water in the feed appears to be mainly related to a blocking effect induced by the presence of relatively large amounts of adsorbed molecular water, limiting access of the reactant molecules to the sample surface for activated generation of the active sites for the process and further reaction. It may be noted that experimental evidences for the deactivating effects of both molecules have basically been related to the partial hindering of generation of active partially reduced copper oxide species active for the process [32]. However, given that carbonate or hydroxyl-molecular water species responsible for such effect can be mainly located on ceria sites, we cannot discard that inhibiting effects on the oxidation activity are partially or alternatively related to issues involving hindering of oxygen activation or transport of activated oxygen species to the active sites, according to proposals for the basic role of the ceria support as oxygen-handling component in the scientific literature [6,10,19].

Acknowledgments

D.G. thanks the Ministerio de Educación y Ciencia (MEC) for a FPI PhD grant under which his contribution to this work was done. Thanks are due to the MEC (project CTQ2006-15600/BQU), and Comunidad de Madrid (project ENERCAM S-0505/ENE/000304) for financial support.

References

[1] J.R. Rostrup-Nielsen, J. Sehested, J.K. Norskov, Adv. Catal. 47 (2002) 65.
[2] Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, Science 301 (2003) 935.
[3] G. Avgouropoulos, T. Ioannides, Ch. Papadopoulou, J. Batista, S. Hocevar, H.K. Matralis, Catal. Today 75 (2002) 157.
[4] S.H. Oh, R.M. Sinkevitch, J. Catal. 142 (1993) 254.
[5] J.B. Wang, S. Lin, T. Huang, Appl. Catal. A 232 (2002) 107.
[6] G. Sedmak, S. Hocevar, J. Levec, J. Catal. 213 (2003) 135.
[7] D.H. Kim, J.E. Cha, Catal. Lett. 86 (2003) 107.
[8] N. Bion, F. Epron, M. Moreno, F. Mariño, D. Duprez, Top. Catal. 51 (2008) 76.
[9] Y. Liu, Q. Fu, M. Flytzani-Stephanopoulos, Catal. Today 93–95 (2004) 241.
[10] G. Marbán, A.B. Fuertes, Appl. Catal. B 57 (2005) 43.
[11] A. Martínez-Arias, A.B. Hungría, M. Fernández-García, J.C. Conesa, G. Munuera, J. Power Sour. 151 (2005) 32.
[12] F. Mariño, C. Descorme, D. Duprez, Appl. Catal. B 58 (2005) 175.
[13] A. Martínez-Arias, A.B. Hungría, G. Munuera, D. Gamarra, Appl. Catal. B 65 (2006) 207.
[14] J.-W. Park, J.-H. Jeong, W.-L. Yoon, H. Jung, H.-T. Lee, D.-K. Lee, Y.-K. Park, Y.-W. Rhee, Appl. Catal. A 274 (2004) 25.
[15] M. Jobbagy, F. Mariño, B. Schönbrod, G. Baronetti, M. Laborde, Chem. Mater. 18 (2006) 1945.
[16] E. Moretti, M. Lenarda, L. Storaro, A. Talon, T. Montanari, G. Busca, E. Rodríguez-Castellón, A. Jiménez-López, M. Turco, G. Bagnasco, R. Frattini, Appl. Catal. A 335 (2008) 46.

[17] A. Martínez-Arias, D. Gamarra, M. Fernández-García, X.Q. Wang, J.C. Hanson, J.A. Rodriguez, J. Catal. 240 (2006) 1.
[18] W. Liu, A.F. Sarofim, M. Flytzani-Stephanopoulos, Chem. Eng. Sci. 49 (1995) 4871.
[19] A. Martínez-Arias, M. Fernández-García, O. Gálvez, J.M. Coronado, J.A. Anderson, J.C. Conesa, J. Soria, G. Munuera, J. Catal. 195 (2000) 207.
[20] B. Skårman, D. Grandjean, R.E. Benfield, A. Hinz, A. Andersson, L.R. Wallenberg, J. Catal. 211 (2002) 119.
[21] A. Martínez-Arias, A.B. Hungría, M. Fernández-García, J.C. Conesa, G. Munuera, J. Phys. Chem. B 108 (2004) 17983.
[22] A.N. Ilichev, A.A. Firsova, V.N. Korchak, Kinet. Catal. 47 (2006) 585.
[23] D. Gamarra, A. Hornés, Zs. Koppány, Z. Schay, G. Munuera, J. Soria, A. Martínez-Arias, J. Power Sour. 169 (2007) 110.
[24] M.-F. Luo, Y.-P. Song, J.Q. Lu, X.-Y. Wang, Z.-Y. Pu, J. Phys. Chem. C 111 (2007) 12686.
[25] M.-F. Luo, J.-M. Ma, J.-Q. Lu, Y.-P. Song, Y.-J. Wang, J. Catal. 246 (2007) 52.
[26] A. Pintar, J. Batista, S. Hocevar, J. Colloid Interface Sci. 285 (2005) 218.
[27] M. Manzoli, R. Di Monte, F. Bocuzzi, S. Coluccia, J. Kaspar, Appl. Catal. B 61 (2005) 192.
[28] G. Avgouropoulos, T. Ioannides, H. Matralis, Appl. Catal. B 56 (2005) 87.
[29] J.B. Wang, D.-H. Tsai, T.-J. Huang, J. Catal. 208 (2002) 370.
[30] H.C. Lee, D.H. Kim, Catal. Today 132 (2008) 109.
[31] D. Gamarra, G. Munuera, A.B. Hungría, M. Fernández-García, J.C. Conesa, P.A. Midgley, X.Q. Wang, J.C. Hanson, J.A. Rodríguez, A. Martínez-Arias, J. Phys. Chem. C 111 (2007) 11026.
[32] D. Gamarra, C. Belver, M. Fernández-García, A. Martínez-Arias, J. Am. Chem. Soc. 129 (2007) 12064.
[33] J.W. Park, J.H. Jeong, W.L. Yoon, Y.W. Rhee, J. Power Sour. 132 (2004) 18.
[34] G. Avgouropoulos, T. Ioannides, Appl. Catal. B 67 (2006) 1.
[35] X.Q. Wang, J.A. Rodriguez, J.C. Hanson, D. Gamarra, A. Martínez-Arias, M. Fernández-García, J. Phys. Chem. B 109 (2005) 19595.
[36] A. Badri, C. Binet, J.-C. Lavalley, J. Chem. Soc. Faraday Trans. 92 (1996) 4669.
[37] C. Binet, M. Daturi, J.-C. Lavalley, Catal. Today 50 (1999) 207.
[38] C. Li, Y. Sakata, T. Arai, K. Domen, K.-I. Maruya, T. Onishi, J. Chem. Soc. Faraday Trans. 1 85 (1989) 929.
[39] C. Li, Y. Sakata, T. Arai, K. Domen, K.-I. Maruya, T. Onishi, J. Chem. Soc. Faraday Trans. 1 85 (1989) 1451.
[40] O. Pozdnyakova, D. Teschner, A. Wootsch, J. Kröhnert, B. Steinhauer, H. Sauer, L. Toth, F.C. Jentoft, A. Knop-Gericke, Z. Paál, R. Schlögl, J. Catal. 237 (2006) 1.
[41] C. Binet, A. Badri, M. Boutonnet-Kizling, J.-C. Lavalley, J. Chem. Soc. Faraday Trans. 90 (1994) 1023.
[42] A. Martínez-Arias, M. Fernández-García, J. Soria, J.C. Conesa, J. Catal. 182 (1999) 367.
[43] T. Caputo, L. Lisi, R. Pirone, G. Russo, Appl. Catal. A 348 (2008) 42.
[44] D. Scarano, S. Bordiga, C. Lamberti, G. Spoto, G. Ricchiardi, A. Zecchina, C. Otero Areán, Surf. Sci. 411 (1998) 272.
[45] A. Martínez-Arias, unpublished results.
[46] D. Gamarra, PhD thesis, Universidad Autónoma de Madrid, 2008.
[47] X. Wang, J.A. Rodriguez, J.C. Hanson, D. Gamarra, A. Martínez-Arias, M. Fernández-García, J. Phys. Chem. B 110 (2006) 428.