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An *operando* DRIFTS–MS study on model $Ce_{0.5}Zr_{0.5}O_2$ redox catalyst: A critical evaluation of DRIFTS and MS data on CO abatement reaction

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Abstract

An *operando* study of CO oxidation by $Ce_{0.5}Zr_{0.5}O_2$ catalysts under dynamic conditions was performed using a prototype gas flow DRIFTS reaction chamber coupled with a MS. Previous studies conducted under oscillating CO/O_2 feedstream conditions, allowed the identification of carbonates as the C-containing storage species on the catalyst surface, with their decomposition being the origin of CO_2 evolution dynamics during O_2 pulses.

A deeper comparison of the time-resolved DRIFTS and MS data revealed some differences that were related to the different observation points of the two detectors. Two methods for the determination of penetration depth of IR radiation in catalysts beds were compared and discussed. From the analysis of DRIFTS data, two main pathways for carbonates decomposition were found at the beginning of the bed of the catalysts: one leading to CO_2 and Ce(IV) sites and another to CO and Ce(III). The last one is active only above 673 K. The preference of one pathway against the other is strictly related to the Ce(III)/Ce(IV) ratio that shows strong variation during the entire cycle.

Keywords: $Ce_{0.5}Zr_{0.5}O_2$ catalyst; *Operando* study; DRIFTS data

1. Introduction

The utilization of transient conditions for material testing is particularly valuable, especially in the field of heterogeneous catalysis [1], as perturbations of steady-state conditions is surely one of the most powerful method to study reaction mechanisms. Moreover, improvements in activity and selectivity can be also gained by periodic changes in feed composition [2,3–5].

In situ DRIFT spectroscopy is one of the fundamental tools to investigate structural changes as well as the presence of adsorbed species on heterogeneous catalysts [6]. When DRIFT spectroscopy is coupled to transient techniques, such as gas-flow switching and pulse adsorption, it becomes a particularly effective *operando* technique able to discriminate between active and spectator species under real reaction conditions [1,7–9].

Since many reactions carried out under transient conditions have pulses duration of few seconds, very demanding instrumental needs are required to record DRIFT spectra under real *operando* conditions [10]. Recently we have developed in our laboratories a prototype DRIFTS reaction chamber able to satisfy the instrumental needs necessary to perform *operando* studies on heterogeneous catalysts under plug-flow conditions [11].

The prototype was utilized to study the CO abatement mechanism over $Ce_xZr_{1-x}O_2$ catalysts carried out under oscillating CO/O_2 feedstream conditions for dynamic OSC measurements under simulated three-way catalysts (TWC) working cycles.

$Ce_xZr_{1-x}O_2$ catalysts find applications in TWC due to their high oxygen storage capacity (OSC) that improves the efficiency of CO, NO and HC removal during rich/lean excursion of exhaust gases [12–14].

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Previous results obtained have shown, in addition to the expected CO oxidation by O_2 stored during CO pulse, CO_2 evolution taking place also during O_2 pulse [12]. Data recently collected with our DRIFTS–MS apparatus strongly suggested a reaction mechanism that involves cerium-zirconium carbonates as intermediate species [15].

However, additional and fruitful information can be gained if DRIFT spectra are used not only to identify the nature of adsorbed and/or evolved species, but also to analyze the time-resolved profiles of the observed IR absorptions.

Here, we would like to show the results that come from a deep comparison of DRIFTS and MS data collected on a $Ce_{0.5}Zr_{0.5}O_2$ model catalytic system, that point out how the complementarity of the two techniques allows the "deconvolution" of a quite complex reaction mechanism. As we will show the presence of concentration gradients along the catalyst bed, which are taken as a starting point in this paper, allows a deeper analysis of the mechanism of action of these systems.

2. Experimental

2.1. Materials and instrument equipment

Cerium-zirconium mixed oxide of composition $Ce_{0.5}Zr_{0.5}O_2$ and cerium oxide were provided by Rhodia and their characteristics have been reported elsewhere [16]. The commercial samples were treated as described by Boaro et al. [15] before the activity tests. The surface area of the fresh ceria-zirconia catalyst is 105 m^2/g and it decreases to 26 m^2/g after ageing.

Catalytic runs were performed under fast alternating transient conditions in a DRIFTS homemade cell built in Inconel 600^{TM}. The cell is linked to a multigas feeding line [11].

DRIFT spectra were recorded on a Digilab FTS-60 spectrometer equipped with a KBr beam splitter and a N_2 cooled linearized broadband MCT detector operating between 400 and 4000 cm^{-1}. This instrument can record good quality spectra in less than one second (three scans collected at 4 cm^{-1} resolution).

The gaseous products were detected downstream by an on-line quadrupole mass-spectrometer (Leda Mass 0–200 amu, enclosed source).

2.2. DRIFT–MS catalytic studies

The activity runs were carried out with about 0.12 g of catalyst loaded in the DRIFTS cell over a borosilicate-glass fibre filter (1.0 μm pore size). The sample was activated under O_2 flow (0.05 NL/min) heating from RT to 673 K at 10 K/min. The Temperature Programmed (TP) experiment was performed increasing the temperature from RT to 723 K with a ramp rate of 10 K/min. The ramp was temporarily stopped at 573, 623 and 673 K (10 min for each stop) in order to record for several cycles DRIFTS and MS data under isothermal conditions.

During the temperature program, every 12 s a different gas was fed into the DRIFTS cell at a rate of 0.18 NL/min. The sequence of pulses was CO (4% in Ar), Ar, O_2 (2% in Ar), Ar. Closely spaced IR spectra were collected at each temperature for two transient cycles. DRIFT profiles of IR active species were obtained by integration of bands with linear baselines: (i) CO – integration from 2000 to 2255 cm^{-1}; (ii) CO_2 – integration from 2275 to 2405 cm^{-1}; (iii) carbonates – integration from 1240 to 1690 cm^{-1}. During the whole treatment the channels at *m/z* 28, 32, 40 and 44 were recorded in the fast scan mode.

Information about the sampling depth of the infrared beam was initially obtained recording spectra of thin layers of the $Ce_{0.5}Zr_{0.5}O_2$ placed over beds of boron nitride, which were obtained by pressing the BN powder with a series of calibrated pestles with different depth (1, 0.6, 0.4, 0.3, 0.2 and 0.1 mm). The thickness of the $Ce_{0.5}Zr_{0.5}O_2$ layer is in principle determined by the depth of the calibrated pestles. However, it was quite difficult to load $Ce_{0.5}Zr_{0.5}O_2$ avoiding any perturbation of the BN bed.

The decomposition of superficial carbonates was instead used for the same purpose. A $Ce_{0.5}Zr_{0.5}O_2$ sample was activated in an O_2 (2%)/Ar flow at 723 K at 10 K/min. At this temperature, it was exposed to the sequence CO (4% in Ar), Ar, O_2 (2% in Ar), Ar (like in the TP experiment) for 30 min. The sample was then reduced with a CO (4%)/Ar flow for 30 min and cooled down to 473 K in the same gas. At this temperature, after 10 min of Ar purging, a sequence of O_2 (0.5%)–Ar pulses was fed to the cell. DRIFTS and MS data were collected during oxidation in the same way as for the TP experiment.

3. Results and discussion

As pointed out in the introduction, CO oxidation by oxygen from CeO_2 leading to CO_2 and reduced ceria is a well known process [12,13]. Different hypotheses were proposed to explain the particular pattern of CO_2 evolution during O_2 pulses [17]. In order to gain more insights on this issue, it was necessary to record DRIFT spectra with our prototype cell under *operando* conditions. Now we have a strong confirmation that CO_2 is produced via a carbonate-decomposition pathway [15]. However, in that case, DRIFT spectra were only used to clarify that ceria carbonates act as active species in each step of the catalytic cycle. Here, we will show that a better knowledge on this mechanism can be gained observing the time-resolved evolution profiles of each observable IR species. In particular, these new insights come from the lack of correlation between the evolution profiles, obtained downstream with the QMS, and the profiles extracted by the DRIFT spectra recorded during the same cycles.

To understand the reasons of this lack of correlation, it was necessary to preliminary establish if the observed discrepancies are not caused by some instrumental artefacts. In Fig. 1 are reported the evolution profiles of CO as recorded by the two detectors at 573 K. Recalling that the light-off temperature of this catalyst is ca. 600 K [15], the profiles reported in Fig. 1 represent what can be observed in absence of any catalytic activity. Thus, the very good match of the two profiles showed in Fig. 1 tells us that any lack of correlation is not due to

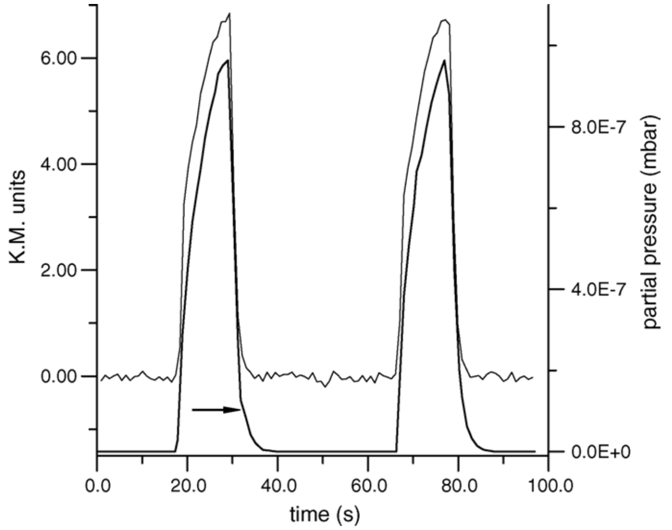


Fig. 1. MS (thick line) and DRIFT (thin line) CO profiles recorded during the transient reaction at 573 K.

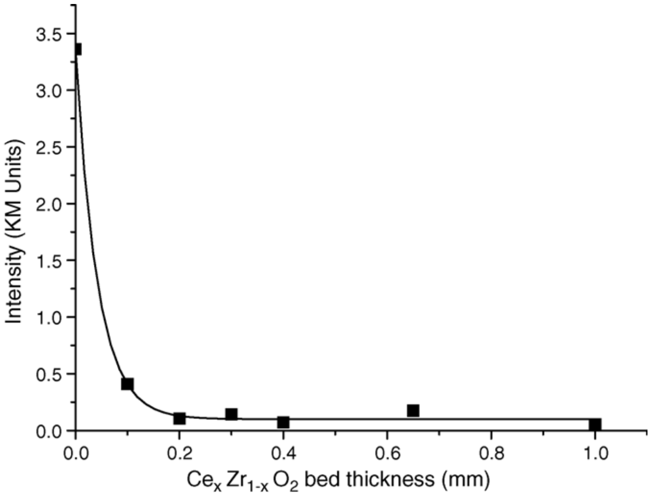


Fig. 2. 1234 cm^{-1} boron nitride absorption intensity recorded versus different thickness of uploaded ceria-zirconia layers.

instrumental artefacts, and that it must be rather correlated with some activity peculiarities of the catalyst.

After some tests conducted varying the reactants composition and flows we have understood that the observed discrepancies are caused by the different observation point of the two detectors. In fact, if we look at the cell geometry [11] we can see that reactants flow from the top to the bottom of the catalytic bed. Considering that the IR beam is focused on the top surface of the catalyst, the DRIFT technique thus "observes" the first layer of the catalytic bed, while the mass spectrometer analyses gases coming out from the bottom of the bed. Although from one side this feature precludes a simple and direct correlation between DRIFTS and MS data, from the other side it could give additional information about the reaction regime as products re-adsorption phenomena.

The question now is: what portion of the entire bed is sampled by the IR beam, or better, which is the penetration depth of the IR beam?

It is well known that the penetration depth depends both on the mirror assembly utilized and on the compound being observed [18,19], meaning that the answer to the latter question cannot be general. We tried to obtain a measure of the sampling depth by two independent methods: by collecting spectra of ceria-zirconia catalytic beds of different thickness over boron nitride (BN) and by an indirect method based on carbonates decomposition by pulses of O_2 of a fully carbonated ceria-zirconia.

BN possess some absorption bands in spectral regions free from catalyst absorptions, so the detection of these bands as a function of the ceria-zirconia bed thickness should be a clear indication of the sampling depth of the DRIFT technique.

As it is evident from data reported in Fig. 2 BN bands disappear when ceria-zirconia bed is 0.2 mm thick, so it is possible to estimate the sampling depth at a value between 0.1 and 0.2 mm.

However, due to the uncertainty related to the preparation of such thin beds with precise thickness, we decide to validate the result obtained by the previous method by an independent one.

Considering that ceria-zirconia carbonates on the surface are stable at 473 K only in an inert atmosphere, while they rapidly decompose under O_2 to yield CO_2, we can use a series of pulses of O_2 on a fully carbonated ceria-zirconia sample to estimate the sampling depth. In fact, using both the FTIR and the MS to detect evolved CO_2 during the O_2 pulse we can say that the fraction:

$$\frac{\text{last IR visible } CO_2 \text{ evolution}}{\text{last MS visible } CO_2 \text{ evolution}}$$

multiplied by the entire bed thickness represents an estimation of the sampling depth of the IR beam. In Fig. 3 is reported the result of such experiment. DRIFTS data evidence that only during the first O_2 pulse CO_2 evolution is detected while the MS detects CO_2 until the 20th pulse. It should be underlined that CO_2 is not detected by MS at the beginning because both carbonates and reduced ceria-zirconia sites are present on our

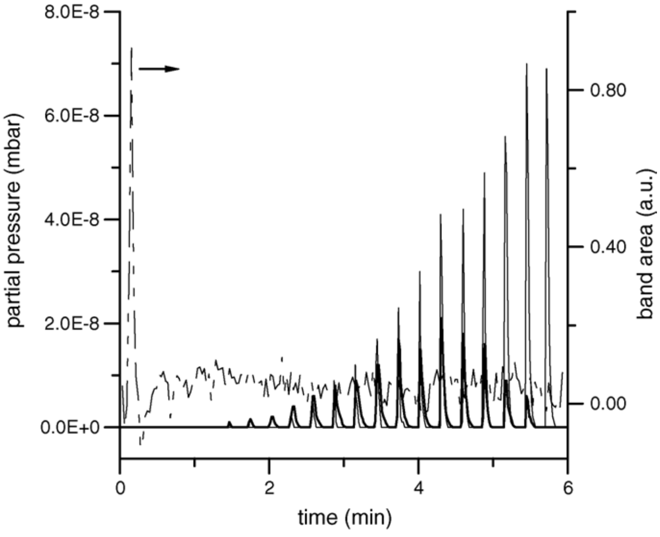


Fig. 3. MS CO_2 (thick line) and O_2 (thin line) profiles and DRIFT CO_2 profile (dashed line) recorded during oxidation at 473 K.

sample. O_2 pulses cause the release of CO_2, as detected by IR, but it is re-adsorbed on Ce(III) sites already present in deeper layers of the catalyst bed, since the amount of oxygen supplied in each pulse is not enough to fully re-oxidize all Ce(III) sites. Only when almost all ceria-zirconia layers are re-oxidized, CO_2 evolution from the catalytic bed will take place and CO_2 will be detected by MS. Taking into account that the total bed thickness is 3.4 mm, the experiment reported in Fig. 3 indicates an IR sampling depth of less than 0.17 mm. From another point of view this fact means also that DRIFT spectra recorded under *operando* conditions relate to the catalytic behaviour of less of the first 1/20 of the total catalyst loaded. Thus, DRIFTS data tell us something different from the overall activity of the catalysts, as detected by the MS. DRIFTS data relate to the reactions that take place at the beginning of the catalyst job, that may be rather different from the overall activity. Let us see why.

For the transient experiment we have indefinitely repeated the cycle reported in the experimental section at various temperatures. In order to exclude any role of CO traces in CO_2 production during O_2 pulse any CO–O_2 mixing should be avoided. Thus, an Ar pulse was inserted between CO and O_2. For the same reason an inert gas pulse between CO and O_2 was also used in activity run measurements [12,13].

DRIFT spectra, collected every second during the whole duration of several cycles, show the presence of various bands in the carbonate region between 1700 and 1200 cm^{-1} (Fig. 4).

According to the literature [20–24], we could assign IR adsorptions as it follows. A sharp band relative to a carbonates stretching mode $\nu(CO_3)$ is observable at 1540 cm^{-1} with shoulders at 1560, 1575 and 1645 cm^{-1} that correspond to bidentate species. Bands located at 1645 and 1470 cm^{-1} could be attributed also to hydrogen carbonates stretching modes $\nu(HCO_3)$ since a well-defined δ(OH) peak of hydrogen carbonates is also visible at 1220 cm^{-1}. A broad adsorption is observed at 1502 cm^{-1} for carbonates. The infrared spectral pattern in the region between 1470 and 1300 cm^{-1} shows a more complex set of peaks. It is clear anyway the presence of two main groups of bands: the first one evidences a maximum at 1425 cm^{-1}, that can be relate to polidentate carbonate, and a peak at 1398 cm^{-1}, the latter is composed by a sharp band at 1360 cm^{-1}, with shoulders at 1379 and 1369 cm^{-1}, overlapping with an adsorption at 1340 cm^{-1}. These last bands refer to bridged and bidentate carbonate species. Of course CO_2 and CO can be also detected by their roto-vibrational bands.

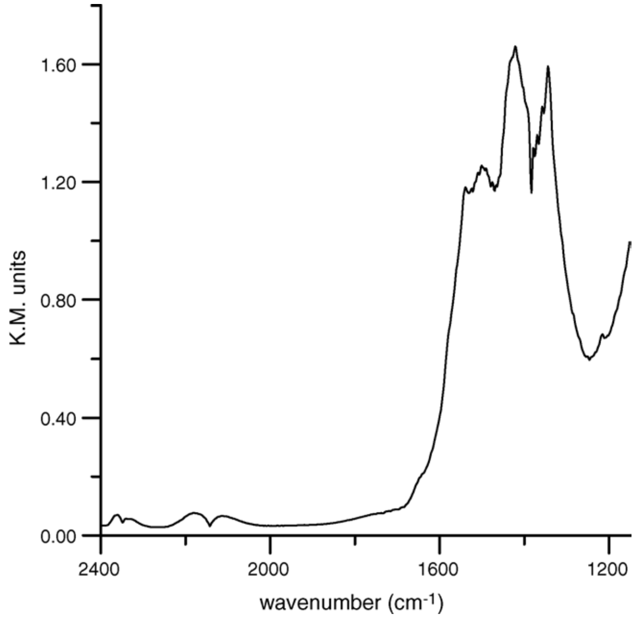


Fig. 4. $Ce_{0.5}Zr_{0.5}O_2$ spectrum recorded during the CO pulse at 673 K.

All bands reported in Fig. 4 show significant oscillations during the entire reaction cycle.

Since hydrogen carbonates bands have a two to three orders of magnitude lower intensity (measured on 1645 and 1220 cm^{-1} ones) respect to carbonates ones it is evident that they play only a minor role in CO adsorption mechanism. Moreover, they show oscillations that closely parallel those of carbonates at low temperatures and that decrease, according to low thermal stability, at higher ones. For these reasons their behaviour will be not further considered in the discussion and will not be included in the proposed mechanism. In the OH stretching region three bands located at 3741, 3651 and 3507 cm^{-1} are observable. While the first and the last band do not vary their intensity during the cycle, the 3651 cm^{-1} absorptions show a very small variation (2.5% of the band area to be compared with the 60% variation of the carbonates bands). This substantial constancy of the ν(OH) absorptions suggests that probably OH are linked to Zr, to a major extent with respect to Ce. It should be recalled that OH bands on zirconia are expected to fall at very similar wavenumbers [25].

In Figs. 5 and 6 the time-resolved profiles recorded at 673 K are reported, as detected by the MS and by the infrared spectrometer, respectively. The MS CO and O_2 profiles show well-separated CO and O_2 transients, while CO_2 profile is characterized by two broader peaks during both the CO and the O_2 transients. These data completely agree with previous experiments conducted in tubular reactors [15].

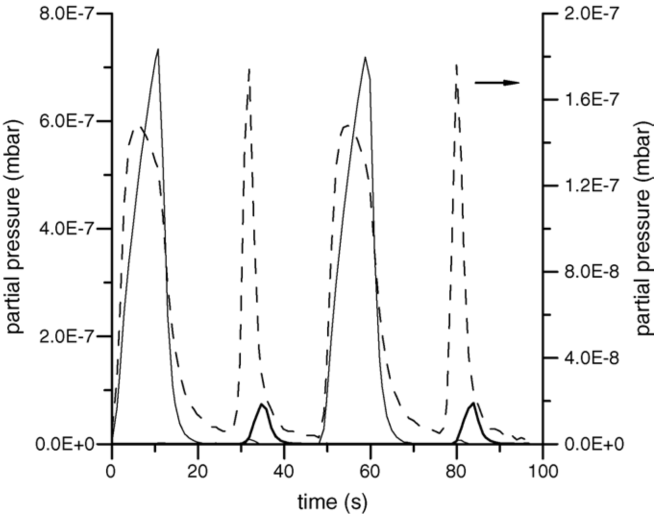


Fig. 5. MS profiles recorded during the transient reaction at 673 K: CO (*m*/*z* 28, thin line), O_2 (*m*/*z* 32, thick line) and CO_2 (*m*/*z* 44, dashed line).

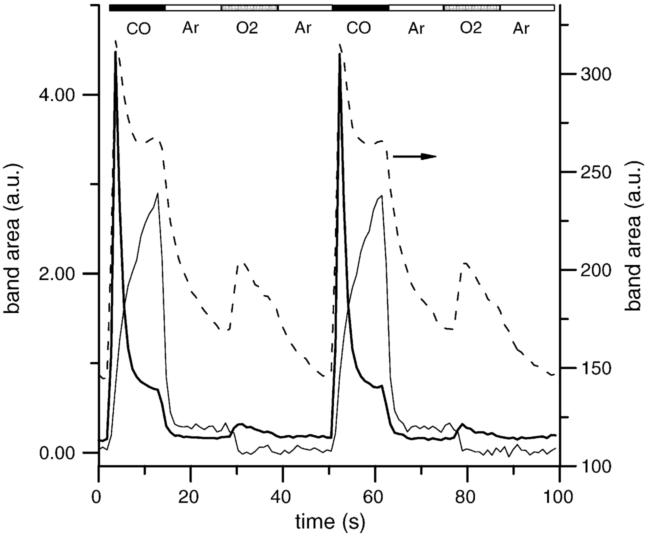


Fig. 6. Peak area trend during two complete Ar/CO/Ar/O_2 cycles at 673 K: CO_2 (2365 cm^{-1}, thick line); CO (2143 cm^{-1}, thin line); CO_3^{2-} (1427 cm^{-1}, dashed line).

Profiles derived from DRIFT spectra are surely more complex (Fig. 6). As a general consideration it can be observed that carbonate bands are always present in every step of the cycle, but a marked variation of the whole set of bands is detectable during each step of the cycle.

At the beginning of the CO step a rapid increase of the carbonates and CO_2 bands is observable: the shape of CO pulse indicates a consumption, which means that CO reacts to form carbonates and CO_2. At the experimental temperature carbonates are not stable and thus decompose to CO_2, as revealed by the MS profiles. Interestingly, both carbonates concentration and CO_2 evolution seem to reach a quasi-stationary condition after some seconds from the beginning of the CO pulse. Anyway the more interesting difference between the MS and the DRIFTS data is that only the infrared spectrometer detects the CO evolution during the incoming Ar step, which is also paralleled by a rapid drop of CO_2 production. These data can be rationalized only invoking the following reactions. For the sake of simplicity we will refer to CZ_{red}, CZ_{ox} and CZ-CO_3 as $Ce_{1-x}Zr_xO_{(2-2\delta)}$, $Ce_{1-x}Zr_xO_2$ and $Ce_{1-x}Zr_{\delta}O_{(2-2\delta)}(CO_3)_{\delta}$, respectively.

$$\delta CO_{(g)} + CZ_{OX} \overset{(1)}{\rightleftharpoons} CZ\text{-}CO_3 \xrightarrow{(2)} CZ_{RED} + \delta CO_{2(g)}$$

These reactions account for the observed quasi-stationary condition. It must be underlined that a thermodynamic equilibrium is never reached and the quasi-stationary conditions are related only to the carbonates and CO_2 concentrations of the IR visible layer. Considering that we have a consecutive-reactions pathway, the constant concentration of these species can be rationalized assuming that the system is trying to reach a steady state condition. However, the direct production of CO_2 by reaction of CO with oxidized ceria-zirconia sites, $\delta CO_{(g)} + CZ_{OX} \xrightarrow{(3)} CZ_{RED} + \delta CO_{2(g)}$ cannot be ruled out, especially at the beginning of the CO pulse, i.e. when the concentration of CZ_{ox} sites is the highest.

Once the concentration of CO drops, at the end of the CO pulse, equilibrium (1) rapidly shifts to the left with the production of CO. Actually, it seems that during the Ar pulse, carbonated ceria-zirconia prefers to decompose yielding CO instead of CO_2. Activity runs were also performed at 573, 623 and 723 K in order to verify the effect of temperature on the reaction mechanism. Fig. 7 shows CO DRIFT profiles at all the temperatures studied. As it can be seen the production of CO during the Ar pulse is clearly temperature dependent. In fact, while it is totally absent at 573 K, it becomes more and more important as the temperature rises up to 723 K. This trend indicates that carbonate decomposition to CZ_{ox} and CO is a favoured process only at temperatures higher than 673 K.

The desorption of CO instead of CO_2 is likely to be the consequence of the high reduction degree reached by ceria-zirconia during CO pulse which is higher than that found under inert gas. This allows transient desorption of carbonates as CO with oxidation of the support. In other words, at the end of the CO pulse we are surely in the presence of an excess of reduced ceria-zirconia sites: this excess drives the decomposition of carbonates to the production of CO and CZ_{ox}. This particular condition is immediately lost at the beginning of the O_2 pulse that rapidly shifts the Ce(III)/Ce(IV) equilibrium to the oxidized form. This shift is so rapid that residual CO is instantaneously converted to carbonates, as detected by the raise of their IR absorptions. The processes that happen during the O_2 pulse are so rationalized:

$$CZ_{RED} + \delta/2O_{2(g)} \xrightarrow{(4)} CZ_{OX}$$
$$CZ\text{-}CO_3 + \delta/2O_{2(g)} \xrightarrow{(5)} CZ_{OX} + \delta CO_{2(g)}$$

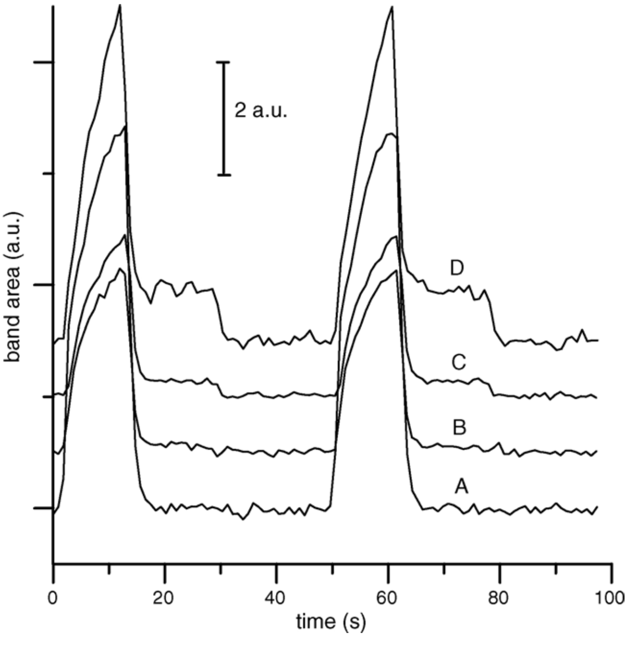
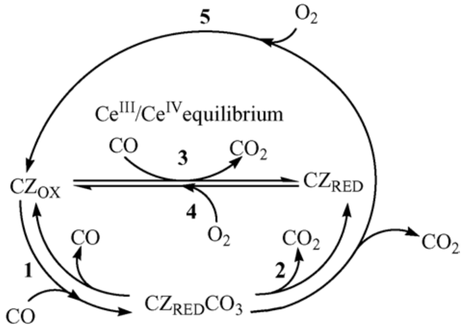


Fig. 7. CO peak area trend during two complete Ar/CO/Ar/O_2 cycles at: 573 K (A), 623 K (B), 673 K (C) and 723 K (D).

During the O_2 pulse oxidation of reduced cerium sites occurs as shown in reaction (4). DRIFT profiles show a CO_2 evolution peak and the depletion of the carbonates bands. The production of CO_2 during the O_2 pulse can be explained assuming that the raise in concentration of CZ_{ox} drives the decomposition of CZ-CO_3 toward reaction (2). Actually also the direct oxidation of CZ-CO_3 (reaction (5)) cannot be ruled out, because it would give the same spectral evidences.

The overall reactivity of ceria-zirconia during the entire cycle, as detected by DRIFTS data is rationalized in the following scheme.



As a final consideration it is important to underline that only on the basis of DRIFTS data here discussed it was possible to derive the mechanism here proposed. It was in fact necessary to observe the place where the concentrations of CZ_{red} and CZ_{ox} are the most variable to detect CO evolution. CO cannot be detected by MS since it is completely stored as CZ-CO_3, when it flows through the lower part of the catalytic bed.

Thus, even if MS data can be fruitfully utilized to study the global system reactivity under transient conditions, they are actually blind about the processes related to the initial reactivity of the catalyst.

4. Conclusions

We investigated CO abatement over $Ce_{0.5}Zr_{0.5}O_2$ in *operando* conditions under fast alternating switching. Although DRIFTS and MS data collected did not directly correlate, this difference permitted us to gain fruitful information on the reaction mechanism. It was so possible to develop a reaction scheme to explain the observed evidences. The relevance of redox equilibrium between oxidized and reduced cerium species was again proved. This particular property of the studied material is found to be the basis of catalytic CO oxidation.

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