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Fast transient infrared studies in material science: development of a novel low dead-volume, high temperature DRIFTS cell

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Abstract

A prototype DRIFTS flow reaction chamber was designed and developed in order to find analytical application in the study of heterogeneous catalysts operating at high temperatures under fast transient gas feed conditions. Minimisation of dead-volumes allows gas replacement in 8–10 s at 10 mL min^{-1} total flow. To overcome problems related to the reactivity of the cell walls under alternating oxidizing/reducing gases, the cell was built with Inconel 600$^{\mathrm{TM}}$, which was tested to be very inert even at high temperatures. The sample holder, which was developed to closely resemble a micro plug-flow reactor, poses some problems in terms of heat transfer to the outer body of the cell (limiting then the maximum reachable temperature) and of the correct measurement of the actual sample temperature. These problems were solved with a careful re-design of the upper part of the cell. The second prototype thus derived is able to reach temperatures up to 803 K and allows gas replacement in less than 4 s at 10 mL min^{-1}. The cell is inserted in a MCT-FT-IR, which allows to collect high quality spectra with a 1 s time-resolution. The downstream flow can be analysed by a quadrupole mass spectrometer equipped with an enclosed source and by a commercial GC. The performances of this prototype cell are presented showing some tests carried out with ceria–zirconia ($\mathrm{Ce}_x\mathrm{Zr}_{1-x}\mathrm{O}_2$) catalysts for CO abatement under real *operando* conditions.

Keywords: DRIFTS; Flow reaction chamber; Ceria–zirconia; CO abatement; Transients studies

1. Introduction

In the last few years the utilization of transient conditions for material testing has grown, especially in the field of heterogeneous catalysis [1]. Besides possible improvements in activity and selectivity generated by periodic changes in feed composition [2], perturbations of steady-state conditions are also of particular interest from an analytical point of view in the determination of reaction mechanisms [3–5]. As an example, perturbations such as gas-flow switching and pulse adsorption, are often particularly valuable to discriminate between active and spectator species [1,6–8].

To gain information about the nature of adsorbed reactants, products and (hopefully) intermediates, different spectroscopic techniques can be used, but infrared spectroscopy is surely one of the most widely utilised [9]. In particular, Diffuse Reflectance Infrared Fourier Transformed Spectroscopy (DRIFTS) should be regarded as the technique of choice, as it allows to record IR spectra directly on solids in powder form, and even with flowing reactant gases passing trough the sample. This advantage over transmission IR techniques should be always carefully weighted against the substantial loss of the collected radiation (95–98% of the incident beam) commonly observed with the DRIFTS technique. This is probably why a lot of catalysts characterisations are still performed on pressed wafers [9–12]. However, this disadvantage has been partially overcome by the availability of commercial high-

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sensitivity MCT detectors, which now allow to record good quality DRIFT spectra with few scans collected. Moreover, due to obvious mass transfer limitations, pressed wafers are not suitable to observe catalysts under real "operando" conditions, which means to observe catalysts under real activity runs, reproducing thus the same catalytic conditions utilised with lab-scale reactors [13].

In any case, as many catalysts of the actual generation work under transient conditions [14–16] and in some cases pulses durations are of few seconds [17], very demanding instrumental needs are required to record DRIFT spectra in these situations. The major requirements needed to study this kind of materials by DRIFT spectroscopy can be summarized as follows:

(i) Fast alternating transient gas feed.
(ii) Transient duration between few seconds and hours with high reproducibility.
(iii) Feed gases of variable and known composition and flows.
(iv) Minimal pressure overshoots and composition changes during feed change.
(v) Minimal gas mixing in the DRIFTS cell during feed change.
(vi) High sample temperature reachable with limited heat transfer to the DRIFTS mirrors compartment.
(vii) High inertness of DRIFTS reaction chamber in oxidizing–reducing atmospheres even at high temperatures.
(viii) Suitable DRIFTS cell geometry to better simulate plug-flow reactors.
(ix) Maintain a high surface of the sample exposed to the IR radiation to avoid excessive beam attenuation.

While the first four points can be accounted for with a proper design and realisation of the gas manifold system, the latter ones directly relates to the design of the DRIFTS reaction chamber. But, in spite of the relevance of this topic, there are no commercially available sample-chambers suitable to satisfy the above-mentioned requirements. One of the most interesting commercial configuration was proposed by JASCO on the basis of the original design of Hattori and coworkers [18], that however does not satisfy points (vii) and (viii) of the previous list, and seems to have a limited temperature working range. SPECAC also offer an interesting solution, but the design of the sample chamber is far from being comparable to a plug-flow reactor.

Various "home-made" sample chambers were thus developed by different groups to overcome these limitations [8,19–21]. Problems generated by the reactivity of stainless steel [19], which is commonly used as building material, were partially compensated by Schubert et al. [21] with an appropriate design of the reaction chamber (i.e. minimising the exposed steel surface). However, if carbon monoxide has to be used as the reactant, iron carbonyls contamination of the sample cannot be avoided, especially working with microporous materials [22], which means that periodic abrasive cleanings of the reaction chamber are necessary.

The same authors have devoted a particular care to simulate a plug flow reactor by lowering the diameter of the sample cup: although this solution is suitable for this purpose (and can also solve many other problems related to the heating system of the reaction chamber), the price paid in terms of IR beam energy loss is so high that minutes are necessary to collect acceptable DRIFT spectra [21], meaning that this cell is not suitable for fast alternating gas feed experiments.

Here we wish to describe the development of two prototypes DRIFTS flow-reaction chambers that was recently carried out in our laboratories to overcome the limitations above described. As we will show, the second prototype was developed to solve most of the problems encountered with the first one. Our prototype DRIFTS flow-reaction chamber should be regarded at least as a deep variation of commercial Harrick HVSR2 DRIFTS cell, even if the "praying mantis" DRIFT mirror set-up from Harrick Scientific Co. was always chosen because of its superior performance in terms of intensity of the collected diffuse radiation, which, as described above, is a valuable parameter.

The performances of the prototype cells are discussed showing the results obtained, under real working conditions, for ceria–zirconia ($Ce_xZr_{1-x}O_2$) CO abatement catalysts that run under fast alternating gas-feed conditions. This catalytic system was chosen to show the analytical performances of the prototype cells because of the extremely short duration (for a catalytic reaction) of gas feed transients, that better emphasises properties and limitations of the proposed DRIFT chambers.

To the best of our knowledge the performances of our second prototype cell, in terms of the unique combination of (i) reachable time resolution, (ii) inertness of the building material and (iii) close similarity to a real catalytic reactor, has no comparison with other commercial and prototype reaction chambers.

2. Experimental

2.1. Apparatus description

In Fig. 1 a scheme of the whole apparatus is shown.

It is composed by four main sections: (1) a gas manifold feeding system; (2) one glass/quartz reactor stand; (3) the DRIFTS cell; (4) the analytical instruments (namely an FT-IR spectrophotometer, a quadrupole mass analyser and a GC). All these parts are connected by heated gas lines (stainless steel tubes, 2 mm o.d.).

The gas manifold allows feed gas mixture switching, by the automatically operated 4-ways crossover valve (Valco 1), between two gas lines, one connected to two MFCs and the other to three MFCs. Each MFC can be fed with one of the four gases chosen by the manually operated 5-ways switching valves.

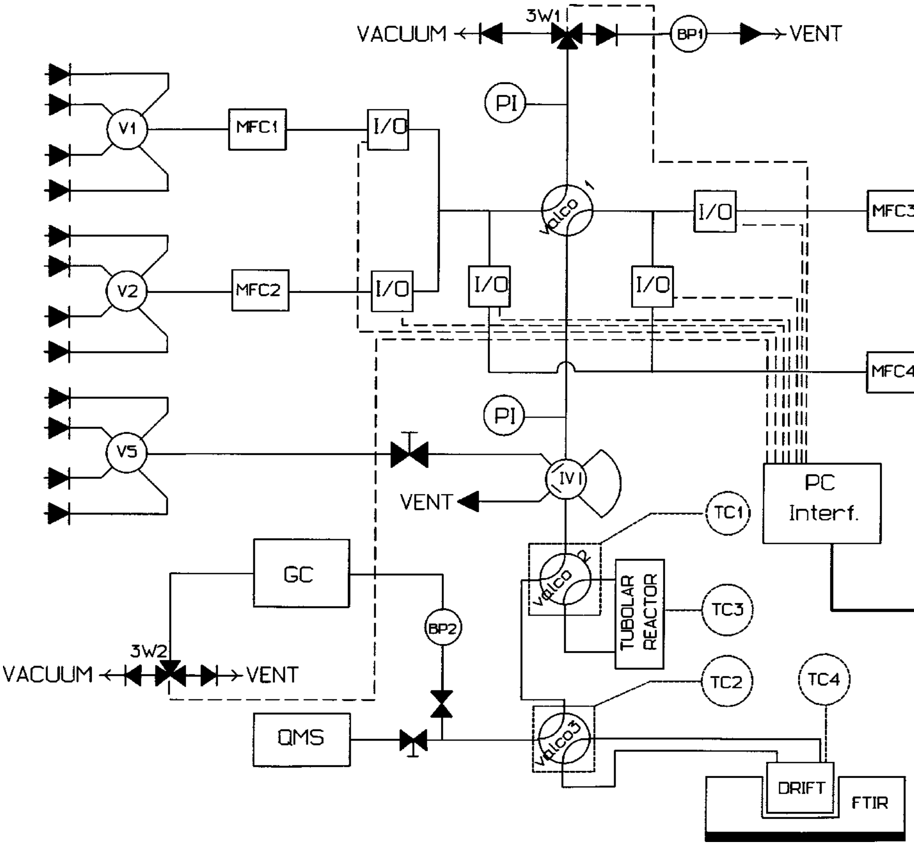

Fig. 1. Scheme of the whole apparatus: MFC1-4 = mass flow controllers (5850 TR series Brooks); I/O = on/off valves, SS AISI 316, 24 V ac, 20 W (Cosmomatic s.r.l.); Valco 1–3 = 4-ways crossover valves, 230 V ac, Valco 2 and 3 are heated (Vici-Valco Instruments); 3 W 1, 2 = 3-ways switching valves SS AISI 316, 24 V ac, 20 W, 20 bar max (Cosmomatic s.r.l.); IV: 6-ways crossover 500 μl injection valve (mod. E90-230 Vici-Valco Instruments); V1-5 = 5-ways switching valves (mod. SS-43ZF2-049 Whitey); BP 1, 2 = back pressure regulators, 0–20 bar; PI = pressure transducer, 30 bar max (mod. TKFE2M3DM Gefran). TC1-4 are chromel–alumel thermocouples connected to: on/off temperature controllers (for TC1 and TC2) and programmable temperature controllers (for TC3 and TC4).

The gas line that is not in use can be evacuated, and/or purged, with the required gas mixture, in order to prepare the feed of the incoming step. The backpressure regulator BP 1 allows to balance pressure drops due to high flows and/or packing of catalyst bed eliminating pressure overshoots during Valco 1 switching. This design of the gas manifold ensures that constant and known composition gases are always delivered to the DRIFTS cell and/or to the reactor.

The five on/off valves, the 3-ways switching valves and Valco 1 are automatically operated, trough a National Instruments interface board (mod. PCI-6024E), by a dedicated software written in Labview 6.1^{TM}. The program is divided in several steps, where it is possible to control the positions of all the valves and the duration of the step itself. The program allows to generate a *n*-steps sequence, which could be replicated *m*-times (*n* and *m* are variables of the program).

DRIFT spectra are recorded on a Digilab FTS-60A spectrophotometer equipped with a KBr beam-splitter and a N_2-cooled linearized broad band MCT detector operating between 400 and 4000 cm^{-1}. The home made reaction chamber fits in a Harrick DRA-2C1 diffuse reflectance accessory.

The volatile products can be detected downstream by an on-line quadrupole mass-spectrometer (Leda Mass 0–200 amu, enclosed source) and by a HP 5890 gascromatograph with gas-sampling valve and with two detectors (TCD, FID). The enclosed source geometry for the QMS was chosen for its superior gas-acceptance capacity, leading to lower limits of detection.

2.2. Material testing

For materials testing Temperature Programmed Decomposition experiments (TPD/CO) were carried out. Clean turnings of Inconel 600^{TM} or stainless steel (AISI 316) were previously calcined for 3 h at 1073 K under pure O_2 flow. Turnings were then heated under CO/He 5% mixture from RT to 673 K at 10 K/min. Gas composition was continuously monitored by the on-line QMS described above.

2.3. Temperature calibration

Temperature calibration (i.e. finding a correlation between actual sample temperature and temperature read by thermocouple) for the second prototype DRIFTS cell was performed by comparing the maximum of CO_2 ($m/z = 44$ mass channel) evolution peak, recorded by the on-line QMS, during Temperature Programmed Oxidative Decomposition (TPOD) experiments carried out both in the DRIFTS reaction chamber and in a tubular quartz microreactor were the TC is dipped in the catalyst bed. The same amount (30–40 mg) of 2% $Pd(acac)_2/SiO_2$ or 5% $Ba(CH_3COO)_2/Al_2O_3$ was loaded in order to keep constant the pseudo-contact time avoiding any kinetics artefact. TPOD were conducted under O_2/(He or Ar) 5% mixture, at different flows (from 20 to 80 mL/min) from RT to 723 K at 5 K/min.

2.4. Analytical performance testing

The analytical performances of the whole apparatus were tested on the CO abatement reaction with $Ce_xZr_{1-x}O_2$ catalysts. Typically about 0.07 g of catalyst were loaded in the DRIFTS cell, and were activated under O_2 flow (0.05 NL/min) increasing the temperature from RT to 673 K at 10 K/min. The activity run was performed increasing the temperature at 10 K/min from RT to 623 K and then keeping this temperature for 10 min. Closely spaced IR spectra at 2 s time resolution were collected, at this final temperature, for two transient cycles. During this activity run, every 10 s a different gas was fed into the DRIFTS cell at a rate of 0.18 NL/min. The sequence of transients was CO (4% in Ar), Ar, O_2 (2% in Ar), Ar.

3. Results and discussion

3.1. Materials testing

Stainless steels, which are commonly used as building materials for DRIFTS cells, are generally too reactive (or the reactants are too aggressive) to be employed at high temperatures under oxidative/reductive alternating atmospheres. As an example carbon monoxide, that is not reactive by contact with well-reduced stainless steel surfaces, acts as a powerful reducing agent by contact with thin film of oxides eventually created by previous high temperature oxidative treatments. We have in fact observed that the AISI 316 alloy used for Harrick DRIFTS reaction chambers is quite prone to oxidation and thus to the formation of $Fe(CO)_5$ upon contact of CO with the oxidised steel walls [22]. The formation of iron carbonyl represents a serious font of sample contamination that is particularly active if micro- and mesoporous materials have to be studied, as they actually behave as powerful carbonyls traps [22,23]. Thus, although the reactivity of the whole steel cell can be minimised by a proper design of the reaction chamber [21], sample contamination by iron carbonyls should be always taken into account especially if long activity runs have to be carried out.

After a preliminary work of material testing on various alloys, we have observed that Inconel 600^{TM}, which is a Ni/Cr-based alloy, shows superior performances (after an high temperature oxidative passivation) in terms of stability to high temperature alternating oxidising/reducing conditions. It should be recalled that Inconel alloys are commonly used for their high resistance to high temperature steams (up to 1173 K) of aggressive acids.

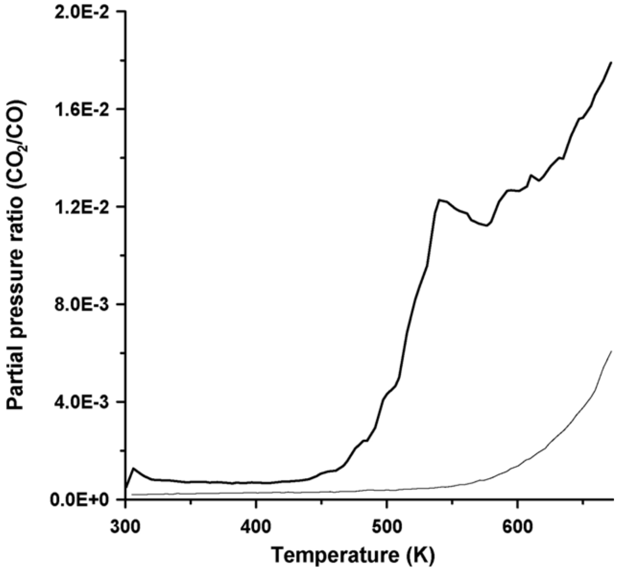

Fig. 2. CO_2 evolution during TPD/CO of Inconel 600^{TM} (thin line) and SS AISI 316 (thick line). Both materials were previously calcined in pure O_2 at 1073 K for 3 h.

In our case, its reactivity was tested on small polished and calcined turnings under CO atmosphere following a typical temperature programmed experiment (see Fig. 2). No $Ni(CO)_4$ or $Cr(CO)_6$ were detected, while a feeble CO_2 evolution starts at 573 K: in any case, the ratio $p(CO_2)/p(CO)$ remains lower than 0.005 even at 673 K. Under the same conditions stainless steel turnings lead to a more pronounced CO_2 evolution that starts at lower temperatures (about 180 °C), and the ratio $p(CO_2)/p(CO)$ is equal to 0.02 at 673 K. On the basis of these results we decided to build our prototype cell using the Inconel alloy.

3.2. Development of prototype DRIFT cells

In Fig. 3 drawings of the first prototype DRIFTS cell are shown. Even if our cell design is different from Harrick HV-DR2 model the outer dimensions of the whole cell were kept similar to Harrick HV-DR2 cell in order to maintain the compatibility with the “Praying Mantis” mirrors device (DRA-2C1 from Harrick). Moreover we also kept the old Harrick closing window system: ZnSe hemispherical window (item H in Fig. 3) stainless steel dome and ring nut (items not shown in Fig. 3 for the sake of clarity) since it allows to have low dead-volumes coupled to sufficient inertness (only ZnSe exposed to reactive mixtures and not stainless steel, like in current Harrick model).

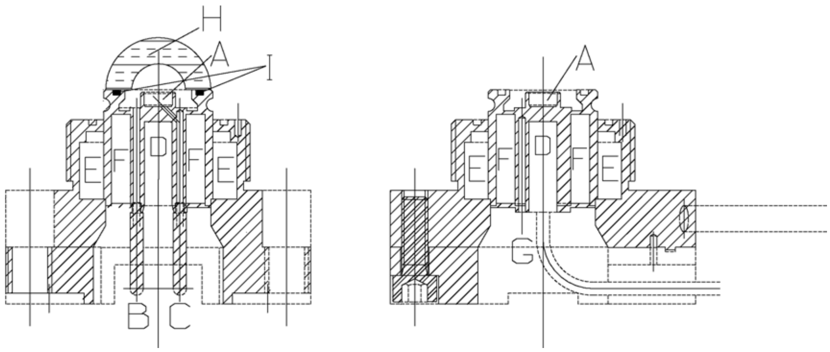

Fig. 3. Drawings of the whole cell, two vertical sections at 90°. A: sample cup (6 mm i.d. × 5 mm height); B: inlet gas tubing; C: outlet gas tubing; D: heating cartridge housing (125 W); E: water flow cooling jacket; F: void space; G: thermocouple housing; H: ZnSe Harrick hemispherical window; I: Kalrez O-ring.

The bottom heating option was decided to have a high IR-exposed surface (that means a high energy of the diffused radiation), and thus to record good quality spectra in short times during transients. A solution similar to those reported by Schubert et al. [21] was not suitable, as the sample holder, wrapped with the heating ring, has an upper surface too small, which results in a low intensity diffused radiation.

With respect to the original Harrick DRIFTS chamber designs, two major differences can be observed. First of all, in the Harrick chamber the inner cylinder with the sample cup and the heating cartridge is fixed to the outer body in its lower position, which implies the presence of high cell dead-volumes: as the result complete gas replacement (better than 99%) is accomplished in about 45 min with a 10 ml/min flow. The presence of a gas-tight diaphragm between the inner cylinder and the outer one in the upper part of the cell and the use of Harrick ZnSe hemispherical window induce a substantial reduction of dead-volumes (down to 2 cm^3) that, as we will show later, allows gas replacement for this prototype in about 8–10 s.

The second main difference concerns how the reactant gases are supplied to the sample. In the Harrick cell gases pass from the bottom to the top of the sample cup and, in order to avoid unwanted sample bed raisings, the inlet gas tube is only loosely attached to the inner cylinder. This solution is quite unhappy for quantitative measurements, as it is not possible to predict how much of the gas inlet-flow actually passes through the sample. With the reversed flow direction adopted in our cell the whole gas flow passes through the catalyst bed, mimicking thus a plug-flow reactor. This solution also allows to use high flow rates (i.e. short contact times or high gas hourly space velocities) without substantially perturbing the catalyst bed.

However high flow rates cause strong limitations in the utilisation of this prototype, due to the cooling effect that feed gases themselves exert on the cell. This unwanted gas-cooling has two main drawbacks. First of all, as the thermocouple is quite far from the sample cup, temperature gradients up to 210 K (which strongly depend on the kind and on the flow rate of feed gases) were recorded. This means that for every experimental condition the thermocouple readings should be carefully calibrated in order to have a correct estimation of the sample temperature. Secondly, the maximum reachable temperature decreases as the cooling effect increases: as an example at 0.18 NL/min of Ar it is not possible to work over 600 K.

To solve these problems we decided to re-design the upper part of the cell (Fig. 4) performing two main modifications to the original project of the first prototype: (i) the thermocouple is placed in much closer contact to the sample and (ii) the diaphragm position is substantially changed. With respect to this latter point we have realised that the position of the diaphragm in the first prototype was quite unhappy as it causes heat losses between the heating cartridge and the sample cup. In the second prototype the substantial raising of the diaphragm allows a more direct heat transfer from the heating cartridge to the sample cup, that minimises the unavoidable cooling effects of flowing gases. It should be mentioned that to obtain such a diaphragm it was necessary to use a combination of a micro-lathe (with home-made cutting tools) and of an electro-erosion machine.

Other modifications were also adopted with respect to the original Harrick project. Namely, the dimensions and the shape of the water-cooling jacket were revisited in order to ensure a better cooling of the upper O-ring. Also the heating cartridge housing was changed to limit the over-heating of lower part of the cartridge.

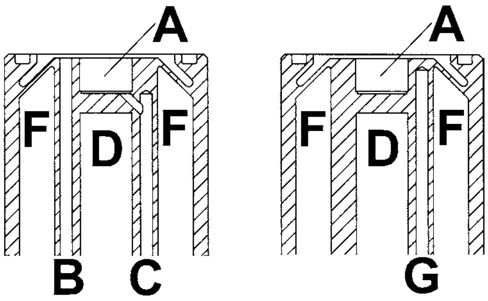

Fig. 4. Drawings of the prototype 2 sample compartment, two vertical sections at 90°. A: sample cup (6 mm i.d. × 5 mm height); B: inlet gas tubing; C: outlet gas tubing; D: heating cartridge housing (125 W); E: water flow cooling jacket; F: void space; G: thermocouple housing.

As a final consideration, the only common features between the commercial and the prototype cells, are related to the utilisation of the same ZnSe hemisphere, and to fact that the outer dimensions are similar as both cells must fit into the praying mantis mirrors assembly.

3.3. Calibration of the prototype DRIFT cell

The most critical step in interfacing the prototype DRIFT chamber with an on-line gas analysis system is to balance the response times of the two detectors. It is essential to parallel the changes in the IR spectrum of the sample with the composition of the gas phase as a function of the increasing temperature. Thus the balance of the response times of the two techniques has to be checked against a suitable reference material in order to calibrate the whole instrument. Ideally this reference material should posses a simple one-step decomposition chemistry:

$$A(s) \rightarrow B(s) + C(g) + D(g)$$

To yield a product B directly correlated with a variation of at least one IR absorption and one or more volatile products (C and D), so the depletion of the IR bands would be directly related to the gas composition. The oxidative decomposition of $Pd(acac)_2$ supported on SiO_2 (Pd = 2%, w/w) satisfies all these requirements as the depletion rate of various acetylacetonate IR absorption bands directly correlates with the evolution of CO and CO_2, which can be easily detected with the $m/z = 44$ channel of the mass spectrometer according to the following stoichiometry [24]:

$$Pd(acac)_2(s) \rightarrow PdO(s) + CO(g) + CO_2(g) + C_xH_yO_z(g)$$

Preliminary experiments have shown a 55–60 s delay of the response of the MS detector at 10 mL/min of gas flow. After various tests, this delay was ascribed to the high dead-volume of the high-precision sampling metering valve located at the inlet of the mass spectrometer. The problem was solved with the utilisation of a low dead-volume metering valve, that however is not as precise as the first one. In any case the gas-sampling precision is not affected by this choice, because the aperture of this valve is always decided on the basis of the pressure detected downstream by a Pirani gauge. The fine tuning obtained with this modification is shown in Fig. 5, where the response of $m/z = 44$ channel (thick line), and depletion rate of the 1520 cm^{-1} IR absorption band (thin line) calculated as $-(I_m - I_{m-1})/(t_m - t_{m-1})$, where I is the band intensity in K.M. units of the mth or $(m-1)$th spectra at and t the time at which the spectra were recorded, each value of depletion rate is plotted against the mean of the corresponding sample temperature $((t_m + t_{m-1})/2)$ which clearly indicates that the responses of the two detector are well balanced, the time resolution was of 1 min both for MS and IR data (i.e. temperature resolution of 5 K). The time resolution was of 1 min for MS (i.e. temperature resolution of 5 K), while the IR spectra were manually collected every 1–2 min.

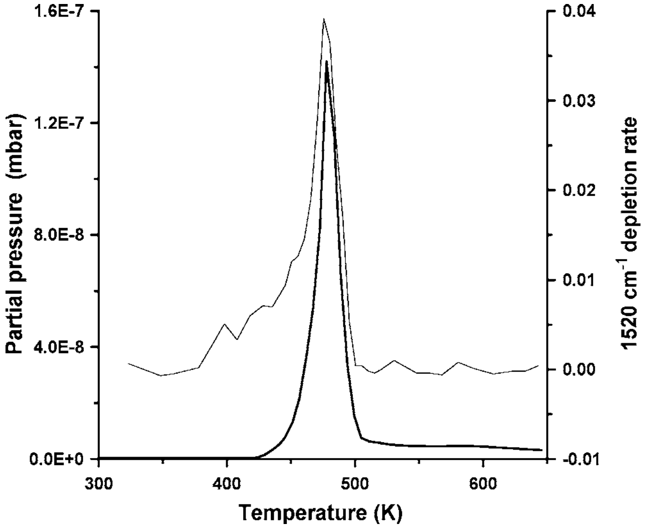

Fig. 5. Temperature programmed oxidative decomposition of $Pd(acac)_2/SiO_2$ (80 mL/min of O_2/He mixture, ramp rate = 5 K/min): response of $m/z = 44$ channel (thick line), and depletion rate of the 1520 cm^{-1} IR absorption band (thin line).

As the cell thermocouple is not dipped into the sample bed it is also essential to calibrate the recorded temperature against the actual temperature of the sample bed. To do this we have compared the temperature programmed decomposition profiles of $Pd(acac)_2/SiO_2$ (Pd = 2%, w/w) obtained with the DRIFTS cell with the same profiles obtained with a tubular reactor, where the thermocouple is dipped into the sample (Fig. 6A). This comparison can be used as a mid-temperature calibration point, while the decomposition of $Ba(CH_3COO)_2$ supported on Al_2O_3 (Ba = 5%, w/w) was used to obtain high temperature calibration points. It is in fact known that $Ba(CH_3COO)_2/Al_2O_3$ decomposes to yield $BaCO_3$ around 703 K according to the following mechanism [25]:

$$Ba(CH_3COO)_2(s) + 4O_2(g) \rightarrow BaCO_3(s) + 3H_2O(g) + 3CO_2(g)$$

Three high temperature decompositions were performed using different gases and different flows in order to observe the influence of the gas-cooling effect. As it can be seen in Fig. 6B–D in all cases the evolution profiles obtained with the DRIFT cell have maxima at slightly lower temperatures but this shift does not depend from the different flow condition.

In any case a plot of maxima of CO_2 peaks during decomposition conducted in tubular reactor and inside our reaction chamber (Fig. 7), reveal a very good linear relationship between the sample temperature and the thermocouple readings ($T_{SAMPLE} = 0.925T_{DRIFT} + 2.18$).

3.4. Performance testing

To exploit the performances of the whole apparatus here we show the data obtained on a real system: $Ce_xZr_{1-x}O_2$ catalysts operating under transient feed of CO/O_2.

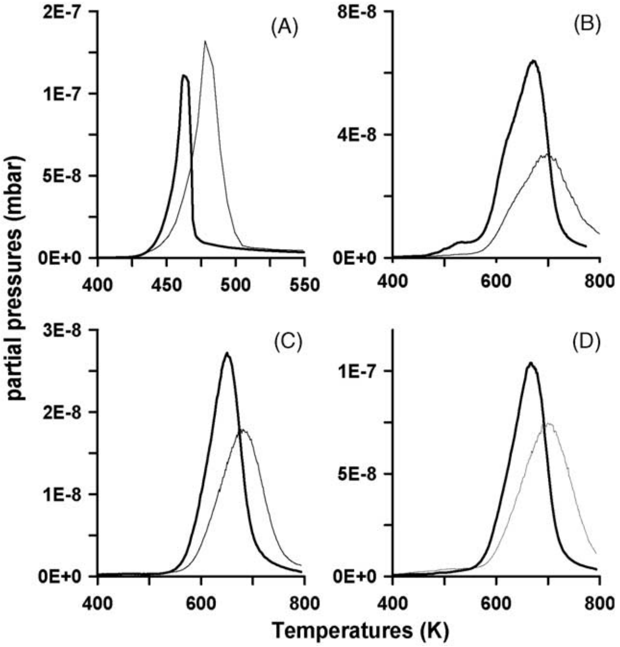

Fig. 6. Comparison of temperature programmed decompositions of $Pd(acac)_2/SiO_2$ (A) and $Ba(CH_3COO)_2/Al_2O_3$ (B, C, D) carried out with a plug flow reactor (thick line) and with the DRIFT cell (thin line) in different flow conditions: A = O_2(5%)/He 20 mL/min; B = O_2(5%)/Ar 20 mL/min; C = O_2(5%)/He 80 mL/min; D = O_2(5%)/He 20 mL/min. All profiles are related to the *m*/*z* = 44 channel (CO_2) of the mass spectrometer.

$Ce_xZr_{1-x}O_2$ catalysts find applications in three-way catalysts 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 [26,27]. Although the data collected with this apparatus were fundamental to elucidate the mechanism of action of this catalytic system [28], here we would like to discuss these data in terms of analytical performance. This catalytic system was chosen to analyse the performances of our prototype cells because of the fast transient nature of the feed gas mixture.

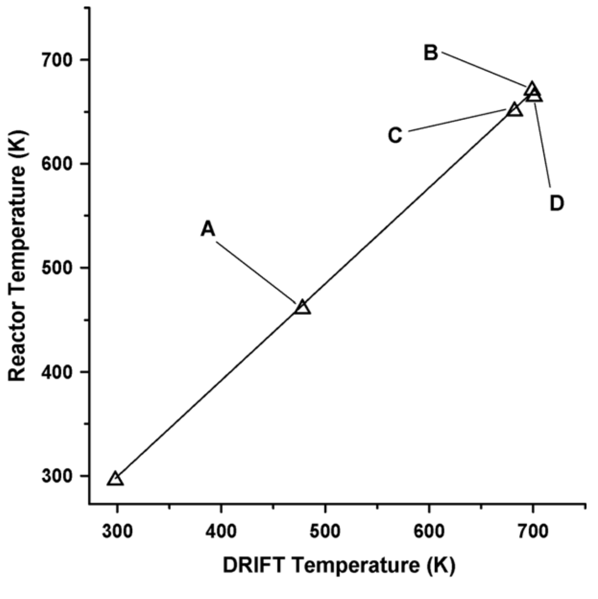

Fig. 7. Plot of temperature of peaks maxima, CO_2 (*m*/*z* = 44), recorded during $Ba(CH_3COO)_2/Al_2O_3$ and $Pd(acac)_2/SiO_2$ decompositions inside the tubular reactor and the DRIFTS cell: labels are referred to the conditions reported in Fig. 6.

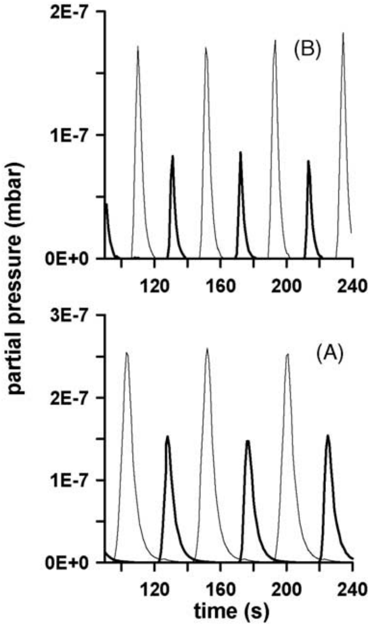

Fig. 8. MS profiles recorded at room temperature during sequences of O_2/CO transients. A: first prototype; B: second prototype. Thick line *m*/*z* = 32 (O_2); thin line *m*/*z* = 28 (CO).

Fig. 8 shows a repeated sequence of CO/O_2 transients, as monitored by the mass spectrometer, recorded with the first and the last prototype. As it can be seen fast gas replacements and a good reproducibility of transients under real working conditions are attained. With respect to the Spectratech DRIFTS chamber that proves to be excellent under transient conditions [29], our first prototype DRIFTS chamber shows a 3–4-fold better time-resolution. With this first prototype the gas replacement is complete (>95%) in about 8–10 s. The last prototype performs even better (Fig. 8B), as the gas replacement is complete in less than 4 s. These results are the direct consequence of the efforts devoted to dead-volumes minimisation.

From the MS profiles shown in Fig. 8 we can say that, if mixings of subsequent gases have to be avoided (better than 95%), the first prototype works properly with transient frequencies up to 0.1 Hz. With the last prototype it is possible to work with transient frequencies up to 0.2 Hz.

Since a partial reduction of oxidised Inconel should be expected under CO at high temperatures, a blank experiment with the empty cell was performed to establish if the amount of evolved CO_2 is negligible with respect to catalytic activity. In Fig. 9 are compared a real high temperature activity run with the blank run. The amount of CO_2 evolved in the blank run is completely negligible.

The great advantages that derive from the possibility to collect DRIFT spectra during experiments as the ones

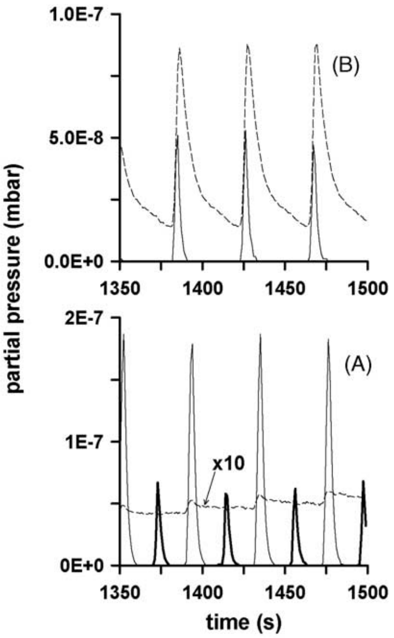

Fig. 9. MS profiles recoded at 723 K for the empty cell, (A) and for the cell filled with $Ce_xZr_{1-x}O_2$, (B) Thick line $m/z = 32$ (O_2); thin line $m/z = 28$ (CO); dashed line $m/z = 44$ (CO_2). In (A) the $m/z = 44$ channel is 10-fold expanded.

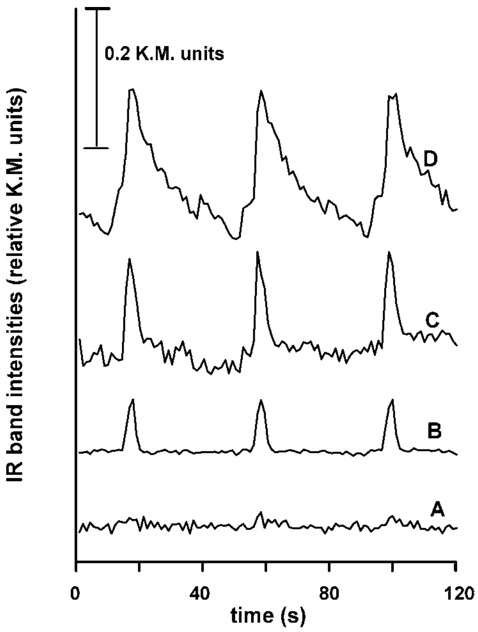

Fig. 10. Evolution of some selected IR band recorded during the transient cycle on $Ce_xZr_{1-x}O_2$ at 723 K (time resolution = 1.12 s, spectral resolution = 4 cm^{-1}, 2 scans collected). A = 1214 cm^{-1}(bicarbonates); B = 2171 cm^{-1} ($CO_{(g)}$); C = 2361 cm^{-1} ($CO_{2(g)}$); D = 1479 cm^{-1} (bridged carbonates).

reported above, rely on the potential information that can be gained about the mechanism of action of the studied materials. Infrared spectra could in fact yield useful insights about: (i) the species responsible of a specific gas evolution; (ii) the "deconvolution" of complex evolution patterns in a combination of simpler reaction steps (iii) the speciation between active and spectator species. As an example the utilisation of such an apparatus was fundamental to clarify that the evolution of CO_2 passes through the formation of bridged carbonates, while bicarbonates acts as spectator species. It was also possible to state that bridged carbonates belong to mixed Ce–Zr surface ensembles and that the previously suggested coke formation is not operative [28].

From an analytical point of view it is instead important to observe if the time-resolution achievable with the FT-IR spectrometer is adequate to study the rapid evolution of adsorbed species and gases. In Fig. 10 are reported some IR bands profiles extracted from the DRIFT spectra recorded during a high temperature transient sequence. The spectra necessary to derive Fig. 10 were collected working with the MCT detector and the "Kinetic mode" available in the spectrometer software Win-Ir Pro^{TM} (two scans collected for each spectrum, with about a 2 s time resolution, no time-delay between spectra).

It is clear that the S/N level is fully acceptable for this kind of experiment and, more generally, it can be said that with this spectrometer setup we can observe bands oscillations down to 0.1 Kubelka–Munk (K.M.) units. Fig. 10 also shows that it is possible to observe even gaseous species which are not adsorbed to any site. Of course, if a better S/N ratio is requested some compromises are necessary, i.e. more scans should be collected (lowering thus the time resolution) and/or a higher spectral resolution should be set.

4. Conclusions

The apparatus described in this work was shown to be suitable to perform transient studies under *operando* conditions. Gas transients of 5 s length can be performed without any mixing or pressure overshoots.

DRIFTS and MS data can be correlated because IR spectra and MS profiles are recorded in the same time scale, allowing to gain fruitful information on reaction mechanisms. This apparatus will be further developed in order to reach a 0.1 s time-resolution of the collected spectra. The utilisation of a step-scan strategy will allow to achieve this target. This development will allow to identify short-lived intermediates and to better describe the reaction dynamics under fast transient conditions.

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