Characterisation of Pt/ceria catalysts by one-pass TPD analysis

François Gaillard

Laboratoire d'Application de la Chimie à l'Environnement (LACE), UMR 5634 CNRS, Université Claude Bernard Lyon 1,
69622 Villeurbanne Cedex, France

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Temperature-programmed desorption of oxygen and carbon dioxide was performed in a single experiment to characterise ceria-based catalysts. The amount of desorbed oxygen provides data on the amount of surface precious metal and their close vicinity. The amount of desorbed CO_2 is related to ceria surface area.

KEY WORDS: ceria; surface area; Pt; dioxygen; carbon dioxide; desorption; TPD.

1. Introduction

Since the introduction, in the early 80's, of oxygen-storing devices for catalysts designed to clean car exhaust, such materials are generally implemented in three-way-catalysts (TWC), that simultaneously oxidise unburned fuels and CO and reduce NO_x [1]. For such a purpose, ceria-based materials are extensively used because of the ability of ceria to easily and reversibly change from Ce^{3+} to Ce^{4+}. This oxygen storage capacity (OSC) was studied by many authors, and is generally assessed by the oxidation of pulsed CO to CO_2 [2,3]. Such studies led to the development of catalysts based on alumina- and zirconia-ceria solid solutions, with improved oxygen mobility, higher OSC, and higher resistance to sintering at high temperature [4,5]. The practical interest is to store oxygen during lean-burn periods and to release it when necessary. The characterisation of ceria-based catalysts is not an easy task and it motivated many studies. Even for simple precious metal (PM)/ceria catalysts, the direct methods to determine the effects of ageing (sintering of the support and of the PM) are scarce. To determine ceria surface, temperature-programmed reduction (TPR) and especially H_2-TPR is generally considered as a suitable technique [6]. TPR profiles of ceria exhibit two peaks, the first one at about 500 °C corresponding to the reduction of surface-capping oxygen while the second one at temperatures higher than 800 °C corresponds to bulk reduction [7]. Rogemond [8] demonstrated that the amount of hydrogen consumed during the low-temperature peak could be related to the ceria surface area. However, some authors [9] showed that the accuracy of such a method is poor and that H_2 adsorption/desorption phenomena are not to be neglected [10]. Moreover, when PM particles are present, the TPR peak related to the reduction of surface ceria is shifted towards lower temperatures and can merge with room temperature H_2 consumption. Therefore, the determination of ceria surface necessitates knowing accurately the amount of exposed PM and the stoichiometry required for the H_2 reduction of oxygen adsorbed onto PM. Then, we tried to develop a technique using a probe molecule more specific for ceria surface. Carbon dioxide could be a good candidate, because it is a molecule used to probe surface basic sites and some studies of its adsorption on ceria are available [11–13]. Moreover, conversely to H_2, its adsorption should not interfere with oxygen atoms adsorbed on PM particles. Consequently, a single temperature-programmed desorption (TPD) experiment should provide much information on the PM/ceria system.

2. Experimental

2.1. Materials

Catalysts were prepared from a commercial ceria (RNL1, from Rhodia) with a purity higher than 99.5%. The main impurity was La_2O_3 (0.3 wt%) and specific surface area (s.s.a.) was 115 m^2 g^{-1}. In order to obtain ceria with various s.s.a., some samples were heated at 2 °C min^{-1} under pure oxygen at a 5 L h^{-1} flow, and then maintained for 4 h at temperatures ranging from about 600 to 1000 °C. The precursor was platinum acetylacetonate ($Pt–[CH–(CO–CH_3)_2]_2$), preferred to the commonly used H_2PtCl_6 precursor which is known to form cerium oxychloride [14] and then to modify surface properties of the support [15]. Ceria samples with various s.s.a. were suspended in a solution containing the required amount of $Pt–[CH–(CO–CH_3)_2]_2$ in toluene to obtain Pt loadings of 0.2 and 2 wt%. The lower loading was chosen in order to minimise adsorption on Pt particles but to let them act as portholes for oxygen [16]. The higher loading corresponds to a classical value for such catalysts. The solvent was evaporated under

E-mail: Francois.Gaillard@univ-lyon1.fr

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reduced pressure, the solid dried for 12 h at 120 °C, crushed and fired under flowing air at 500 °C to perform the precursor decomposition. After cooling down under air and 30 min nitrogen purge, the catalyst was reduced at 500 °C for 4 h under flowing hydrogen (6 L h^{-1}).

2.2. TPD analysis

TPD of oxygen (O_2-TPD) was performed in both flow and vacuum systems. CO_2-TPD was performed with flow system only in order to determine also the amount of CO_2 adsorbed at room temperature.

The device used for TPD in vacuum was described in a previous paper [17]. The catalyst powder (about 100 mg) was placed in a stainless steel sample holder (50 × 10 × 3 mm), supported by a K-type thermocouple (50 μm wires), placed in a quartz reactor. Heating was achieved by a high-frequency system (1.1 MHz, 6 kW, manufactured by CFEI, France) with a 6-turn inductive coil placed outside the reactor. This system allows a fast heating, with a small temperature gradient, of the sample holder that is virtually isolated, thermally and mechanically, from both the reactor and the heating device. The reactor can be evacuated down to 5×10^{-8} Torr by a turbomolecular pump and the mass spectrometer was fitted with its own pumping system down to 1×10^{-7} Torr. Analysis of species released during TPD run was carried out by a quadrupole mass spectrometer (Riber QS100) and data were processed by homemade dedicated software. Catalyst was first evacuated down to 1×10^{-6} Torr at room temperature, and then heated at 1 °C s^{-1} up to 400 °C in pure O_2 at 100 Torr. After 1 h, the reactor was evacuated and the catalyst heated at 500 °C for 1 h, then cooled down to 400 °C and exposed to 20 Torr O_2 for 1 h. Then, the sample was cooled down to room temperature under O_2 atmosphere and then evacuated to 10^{-6} Torr. After that, TPD was performed using a 1 °C s^{-1} heating rate and desorbed molecules were detected from room temperature to 800 °C, following the peaks at $m/e = 18$, 28, 32, and 44 amu, corresponding to H_2O^+, N_2^+ or CO^+, O_2^+ and CO_2^+ ions, respectively.

For flow TPD experiments, about 100 mg of catalyst were placed on a quartz wool bed in a u-shaped quartz reactor, positioned vertically in a programmable tube furnace. Temperature was measured by two K-type thermocouples positioned outside the reactor. Pre-treatment gases were pure He and O_2 at a flow of 1.2 L h^{-1}. The TPD experiments were performed in He medium at a flow 1.8 L h^{-1} monitored by a Brooks mass flow controller. A part of the gas exiting the reactor (about 0.6 L h^{-1}) was sampled by a heated capillary and analysed by a VG Gasslab 300 quadrupole mass spectrometer. Before TPD experiments, samples were heated in pure oxygen stream at 5 °C min^{-1} up to 400 °C, maintained 1 h at this temperature and cooled down to room temperature. Then 1%CO_2/He mixture flow was established, bypassing the reactor, and analysed by the mass spectrometer in order to provide reference signal level for quantitative CO_2 analysis. Then, the mixture was passed through the reactor and the amount of CO_2 adsorbed irreversibly at room temperature was determined. After this adsorption step, the reactor was purged by pure He and at 20 °C min^{-1} up to 800 °C. Signals at $m/e = 16$, 18, 28, 32, 44 amu corresponding to O_2^+, H_2O^+, N_2^+ or CO^+, O_2^+ and CO_2^+ ions, respectively, were recorded.

Analysis by TPR was performed with the same apparatus, using 0.99% H_2/He mixture at 1.8 L h^{-1}. Before the TPR run catalysts were treated as described previously and the reactor flushed 15 min by He. Then H_2 consumption at room temperature was determined and TPR carried out with a heating rate of 20 °C min^{-1}.

2.3. Other physicochemical characterisations

Chemical analysis of Pt was performed by ICP after treatment of the catalyst powder in HCl-HF mixture followed by dissolution in HCl. Specific surface areas were measured according to the BET method by nitrogen adsorption at 77 K on samples previously evacuated 2 h at 300 °C under 10^{-5} Torr and multipoint analysis was performed with a laboratory-made apparatus.

3. Results and discussion

3.1. Catalysts conditioning and characterisation

As shown in table 1, according to the thermal treatment selected in the range from 600 to 1000 °C, s.s.a. can be varied from 115 to 19 m^2 g^{-1}. The amount of platinum deposited is slightly lower than the target value as also reported in table 1. Excepted for ceria pretreated at 594 °C, the calcination and reduction treatments following the impregnation do not lead to an additional decrease of s.s.a.. Further in this paper, the samples will be noted Ce*xx*/*yy* where *xx* is the rounded s.s.a. value and *yy* the target Pt content, i.e. 0.2 or 2 wt%.

Table 1
Characteristics of ceria samples

Sample designation	Treatment temperature (°C)	Pt amount (wt%)	BET s.s.a. (m^2 g^{-1}) prior to/after calcination
Ce	No treatment	No impregnation	115/–
Ce90/0.2	594	0.135	97/92
Ce70/0.2	695	0.180	78/72
Ce60/0.2	800	0.120	59/60
Ce40/0.2	900	0.195	38/39
Ce20/0.2	1005	0.155	20/19
Ce90/2	594	1.845	97/94
Ce20/2	1005	1.865	20/19

TPD profiles of ceria samples as-received, or submitted to mere heating at 500 °C in vacuum, at 400 °C in O_2, or at 400 °C in He exhibit very large CO_2 and H_2O desorption peaks in the temperature range 450–500 °C and a small O_2 desorption peak. Such peaks would definitely mask the desorption of O_2 or CO_2 probe molecules. As reported by Perrichon and co-workers a good solution is to perform alternate treatments in O_2/vacuum/O_2 or O_2/inert gas/O_2. The figure 1 shows the TPD profiles at *m/e* 18 (H_2O) and 44 (CO_2) amu, recorded during heating at 20 °C min^{-1} under pure He (trace a) or pure O_2 (trace b). The heating is limited at 400 °C, in order to modify as less as possible the catalyst under study. Obviously, treatment in He does not lead to a complete elimination of carbonaceous species and of water. Conversely, heating in O_2 flow leads to the desorption of much larger amounts of CO_2 and H_2O, and the baselines for traces at 18 and 44 amu are recovered during the isothermal plateau at 400 °C. These results justify the use of the oxidation/vacuum/oxidation or oxidation/helium/oxidation cycles described in the experimental part. TPD profiles of the ceria supports treated according to this procedure do not exhibit residual CO_2 or O_2 desorption peaks that would be detrimental to the detection of desorbed probe molecules.

The use of TPR by H_2 H_2-TPR is an admittedly valuable method to determine ceria surface area [19]. We performed TPR experiments on the ceria supports with various s.s.a. prior to Pt impregnation. Two hydrogen consumption peaks are observed: one with a maximum at 575 °C and a wide structure at higher temperatures. According to the literature [20,21] the first peak corresponds to the reduction of surface Ce^{4+} to Ce^{3+} and the second one to a bulk reduction. The area of the first peak can be correlated to ceria surface and our results give 4.1 μmol H_2 per m^2 of ceria, very close to the value 3.9 μmol H_2 m^{-2} reported by Perrichon and co-workers [18,22]. When ceria samples are loaded with Pt, the first reduction peak is shifted to lower temperatures

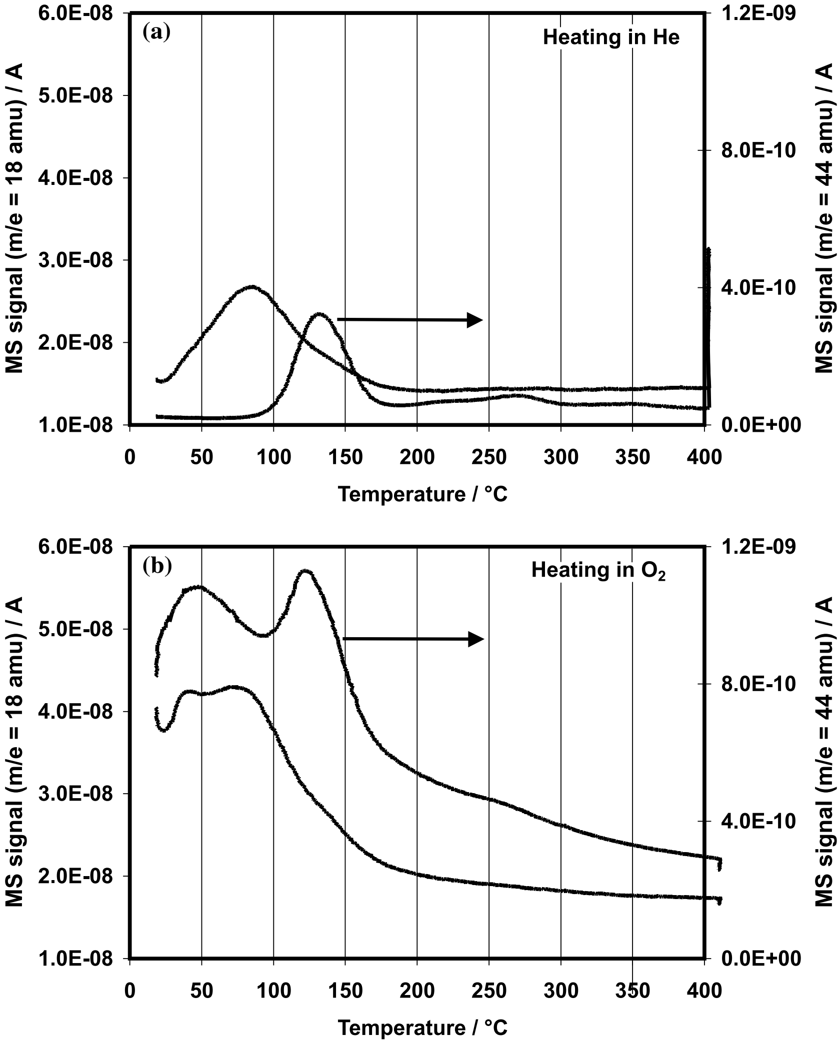

Figure 1. TPD profiles (*m/e* = 18 and 44 amu) of Ce90/2 samples in (a) pure helium and (b) pure oxygen atmospheres.

(maximum at about 70–90 °C). The hydrogen consumption corresponding to this peak is quite low (ranging from 0.18 to 0.58 μmol H_2 per m^2 of ceria) and depends both on ceria surface and Pt loading. The main hydrogen consumption takes place at room temperature. These experiments show the limitations of ceria surface determination by H_2-TPR, because it is necessary to know accurately the PM loading, the percentage of accessible metallic area and the stoichiometry of oxygen adsorption. This observation led us to consider the adsorption of a probe molecule specific to the ceria surface.

3.2. Carbon dioxide and oxygen TPD

Room temperature CO_2 adsorption was performed on Pt-free and -loaded ceria samples with various s.s.a., after the conditioning treatment described in the experimental part. The amount of CO_2 irreversibly adsorbed was determined by a conventional subtraction method. Typical TPD profiles are shown in figure 2 for (a) Ce90/0.2 submitted to CO_2 adsorption, (b) Ce20/0.2 submitted to CO_2 adsorption, and (c) Ce90/0.2 without CO_2 adsorption. A single and quite symmetrical-in-shape peak with a maximum in the range 130–180 °C is recorded, the area of which is related to ceria surface area. A CO_2 desorption peak at 140 °C was also reported by Luo *et al.*, in one of the very scarce papers on CO_2-TPD from ceria [12]. These authors related this peak to the desorption of monodentate carbonate. No CO desorption peak was observed during the TPD run, the small peak at $m/e = 28$ amu, synchronised to the peak at 44 amu, being quantitatively justified by CO_2 fragmentation in the mass spectrometer. For temperatures lower than 400 °C, no interfering TPD peak is observed on a blank sample *i.e.* Ce90/0.2 not submitted to CO_2 adsorption. In figure 3, the correlation is shown between the amounts of adsorbed and desorbed CO_2 and the specific surface area for ceria samples as-received or loaded with either 0.2 or 2 wt% Pt. Linear regression results give a value of 2.8 ± 0.2 μmol CO_2 m^{-2} of ceria, a bit lower than the value 3.05 CO_2 molecules m^{-2} reported by Duprez and Martin [16]. The restitution ratio between adsorbed and desorbed CO_2 amounts generally exceeds 95% for all pre-oxidised samples. Such a good accord between the amounts of CO_2 chemisorbed and thermodesorbed was previously observed by Duprez and Martin [16] for ceria and ceria–alumina solids. Additional experiments were performed on reduced samples and we observed similar TPD profiles and quantitative variation with s.s.a. For such reduced samples, the restitution ratio is lower (about 78%) but this can be explained by a partial CO_2 decomposition at the Pt/ceria interface leading to an extra consumption employed to form CO and to fill oxygen vacancies [23]. The adsorption of CO_2 molecules on oxides at room temperature leads to surface species that depend upon basic sites nature [24]. Hydrogenocarbonates or carbonates formation can be expected, but the first one was ruled out on ceria [25]. From the infrared study of Lavalley and co-workers [26] mono- and bidendates carbonates may be involved and are compatible with the observed desorption temperatures. The formation such species advocates CO_2 to be a direct probe of surface Ce ions.

The desorption of oxygen was investigated either in flow or in vacuum TPD system. Typical profiles are shown in figure 4 for (a) Ce90/0.2 submitted to CO_2 adsorption, (b) Ce90/0.2 without CO_2 adsorption, and (c) Ce90 without Pt loading. The trace at $m/e = 32$ amu exhibits two desorption peaks at about 450 and 620 °C, consistent with two kinds of adsorbed oxygen species

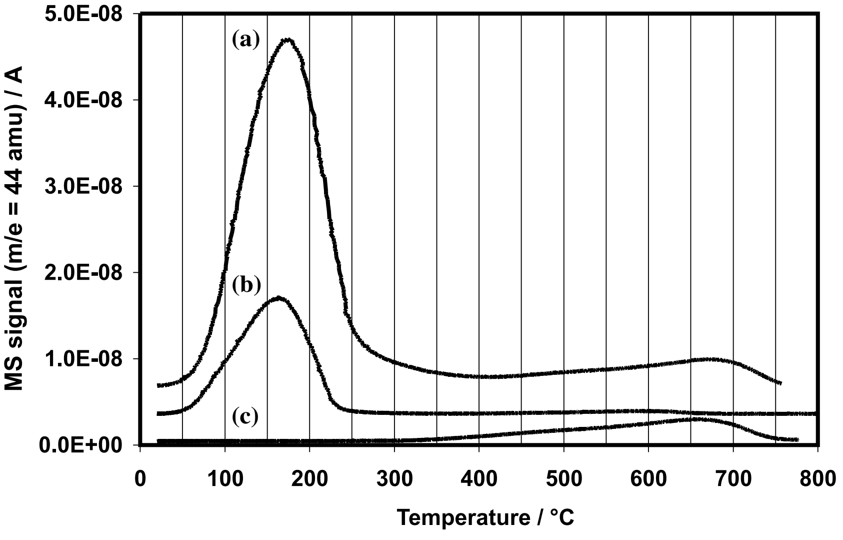

Figure 2. CO_2-TPD profiles of (a) Ce90/0.2 submitted to CO_2 adsorption, (b) Ce20/0.2 submitted to CO_2 adsorption, and (c) Ce90/0.2 without CO_2 adsorption (traces are offset to improve readability).

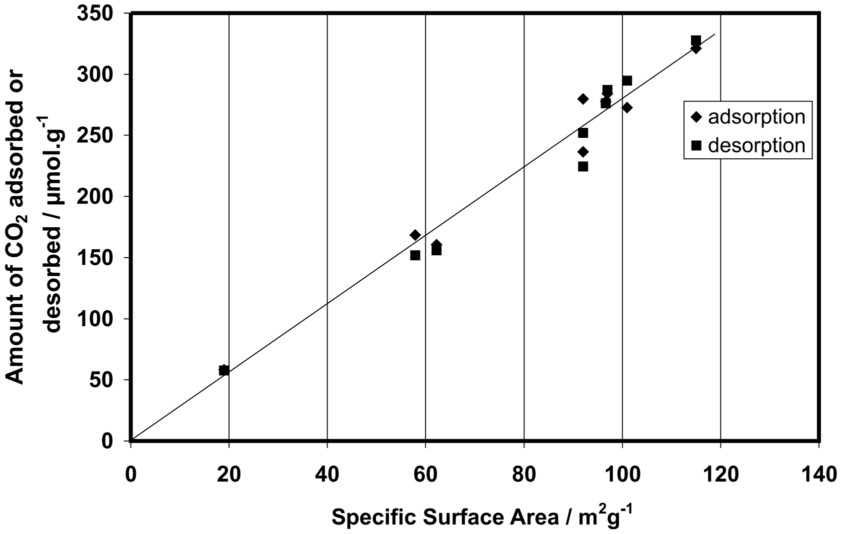

Figure 3. Amounts of CO_2 adsorbed and desorbed versus specific surface area for ceria samples as-received or loaded with either 0.2 or 2% Pt.

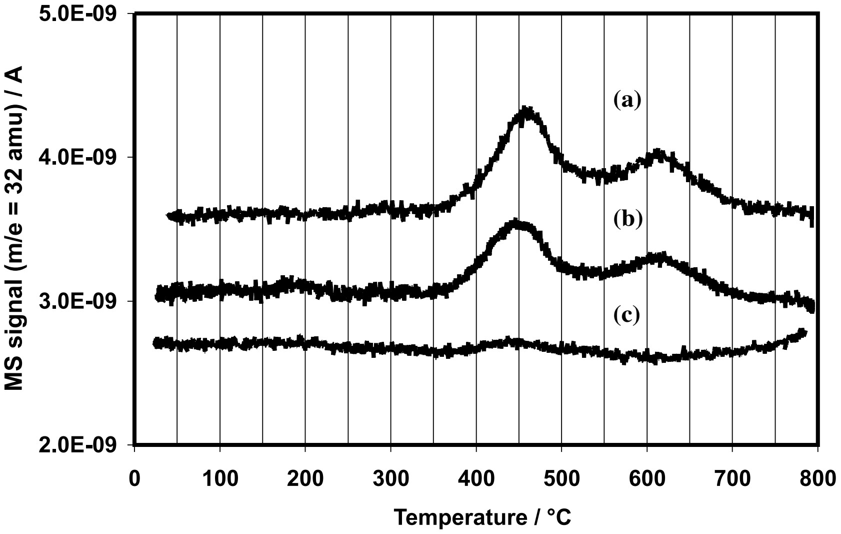

Figure 4. O_2-TPD profiles of (a) Ce90/0.2 submitted to CO_2 adsorption, (b) Ce90/0.2 without CO_2 adsorption, and (c) Ce90 samples (traces are offset to improve readability).

generally reported in the literature [27,28]. The peaks obtained with the vacuum system are shifted towards the higher temperatures and their resolution is lower, mainly because of the much higher heating rate [29]. The shape and area of this double peak are not affected by CO_2 adsorption, this observation advocates for a lack of competition between the CO_2 probe molecule and adsorbed oxygen. It is noteworthy that no oxygen desorption is observed arising directly from the ceria support (trace c), where no Pt atoms are present to act as portholes, as generally described in the literature [16]. In figure 5 are plotted quantitative O_2-TPD results obtained both by flow or vacuum systems. The first observation is that there is no influence of the s.s.a. on the amount of oxygen desorbed. For example, a near-constant value is observed for all the samples loaded at about 0.2 wt% Pt, the desorbed oxygen amounts ranging from 3.5 to 5.5 μmolO_2 per g of catalyst. The differences can be correlated to the exact amount of Pt determined by chemical analysis. The atomic ratio Odesorbed/Pt ranges from 0.9 to 1.3, suggesting that oxygen atoms in the vicinity of Pt particles can participate the desorption phenomenon. Samples loaded to about 2 wt% Pt generate higher amounts of desorbed oxygen, 13.8 and 24.65 μmolO_2 per g of catalyst for Ce20/2 and Ce90/2, respectively. The corresponding atomic ratios Odesorbed/Pt are 0.3 and 0.5. These different values can be explained by different Pt

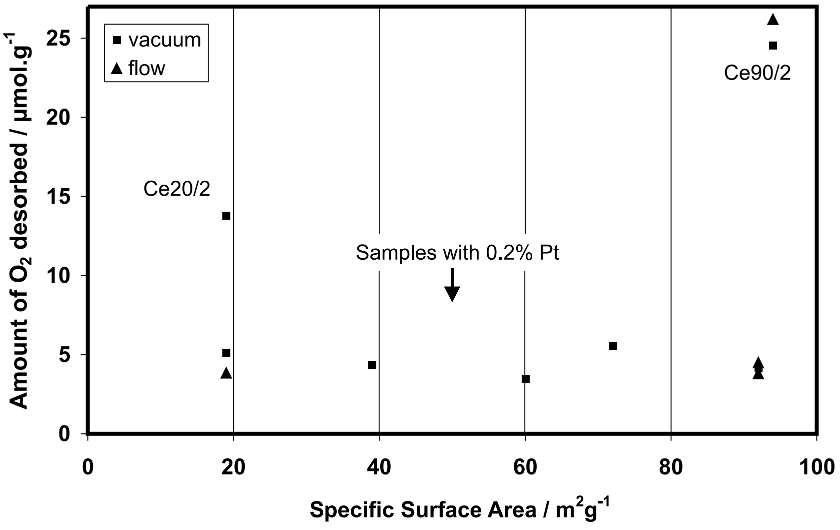

Figure 5. Amounts of O_2 desorbed versus specific surface area for ceria samples loaded with 0.2 or 2% Pt. TPD was performed either in He stream or in vacuum.

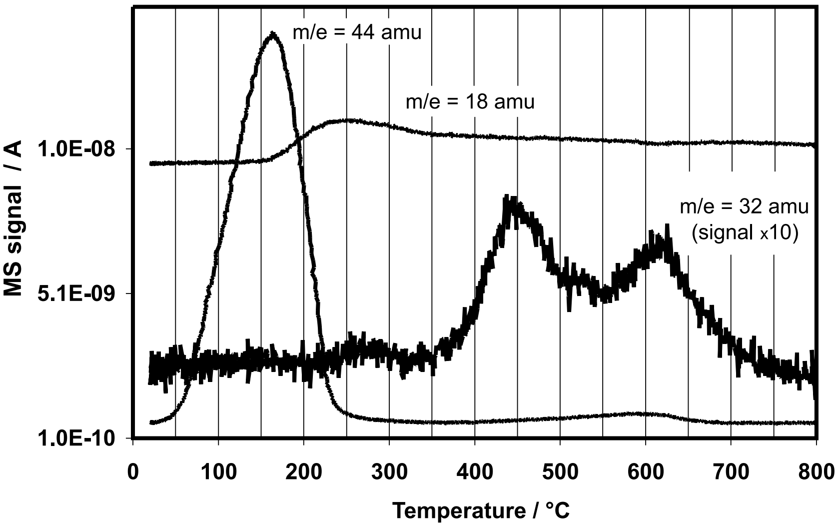

Figure 6. TPD spectra in He stream of Ce20/0.2 sample submitted to CO_2 adsorption. Signals at $m/e = 18$, 32, and 44 amu are reported (traces are offset to improve readability).

dispersion according to the s.s.a. of the support, and as expected the support with lower s.s.a. (Ce20) exhibits a lower Pt dispersion.

As shown by the previous results, no interference occurs between desorption peaks on traces at $m/e = 32$ and 44 uma. The first signal may give qualitative and quantitative information on oxygen available from the catalyst surface, mainly related to Pt particles and possibly their very close vicinity. The second one gives qualitative and quantitative data on the ceria surface area. Such a complete one-pass TPD analysis is illustrated, for Ce20/0.2 sample, in figure 6 were traces of signals at $m/e = 18$, 32, and 44 amu are reported versus temperature. The small CO_2 desorption peak at 440 °C reported by Luo *et al.* [12] and attributed to desorption

4. Conclusions

From this study, we may conclude that CO_2 is a good molecule to probe ceria surface area and that CO_2 adsorption followed by TPD is a good candidate to be substituted to H_2-TPR, especially when platinum is deposited at the ceria surface. In addition, CO_2-TPD may also give indication on surface basicity.

O_2-TPD arises from PM particles and their very close vicinity. Therefore, these data may give information on oxygen species easily available for catalytic reaction. The lack of interference between the two probes allows for a fast and one-pass analysis. This method should be tested for with Ce–Al or Ce–Zr oxide, where both ceria surface area and released oxygen are important for the catalytic properties.

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