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Transient TPSR, DRIFTS-MS and TGA studies of a Pd/ceria-zirconia catalyst in CH_4 and NO_2 atmospheres

L. Zenboury, B. Azambre *, J.V. Weber

Laboratoire de Chimie et Méthodologies pour l'Environnement (LCME), Université Paul Verlaine- Metz,
Rue Victor Demange, 57500 Saint- Avold, France

Abstract

In this study, the parameters governing the activity of Pd/ceria-zirconia catalysts in the selective catalytic reduction (SCR) of NO_x assisted by methane are investigated using a combination of temperature-programmed spectroscopic and thermogravimetric techniques and transient SCR conditions. By DRIFTS of adsorbed CO, it is established that Pd species on $Ce_{0.2}Zr_{0.8}O_2$ are mainly present in cationic form but exhibit high reducibility. As found by temperature-programmed surface reaction (TPSR) in $CH_4 + NO_2$ atmosphere, the CH_4-SCR reaction is initiated at 280 °C on Pd/$Ce_{0.2}Zr_{0.8}O_2$ and yields almost 100% N_2 above 500 °C. DRIFTS-MS and TGA experiments performed under transient SCR conditions show that $DeNO_x$ activity is due to a surface reaction between some methane oxidation products on reduced Pd sites with ad-N_xO_y species presumably located on the support. The detrimental effect of O_2 on $DeNO_x$ is explained by the promotion of the total combustion of methane assisted by the ceria-zirconia component at the expense of the SCR reaction above 320 °C.

Keywords: Ceria-zirconia; SCR; $DeNO_x$; Methane; DRIFTS; MS

1. Introduction

The abatement of nitrogen oxides emissions from stationary power sources and nitric acid installations has been extensively studied during the 30 last years [1,2]. The selective catalytic reduction (SCR) of NO_x by ammonia over $V_2O_5/WO_3/TiO_2$ is practically applied for power plants [1,2]. However, problems associated with the ammonia storage, equipment corrosion or the risk of environmental contamination by unreacted ammonia emissions are the main disadvantages that limit the development of this technology [3]. Therefore, it is very important to find alternative catalytic post-treatments of NO_x emissions. In that respect, the main advantage of the NO_x-SCR by hydrocarbons is the possibility to use a gas mixture very similar to that found at the exhausts of installations [3]. Nowadays, the types of catalysts and reductants studied are extremely variable. Most of the formulations are based on ion-exchanged zeolites and supported metals on various metal oxides [3–6]. However, their deactivation by the water, SO_2 or CO_2 present in the feed are the main disadvantages that limit the development of these SCR catalysts at the industrial scale [1,3,7,8]. In the last decade, ceria-zirconia mixed oxides have attracted much attention due to their high thermal stability, unique redox properties, high oxygen storage capacity and stabilization of noble metal dispersion [9,10]. Very recently, ceria-zirconia was used either as a support or a catalyst for the selective catalytic reduction of NO_x by hydrocarbons [9,11,12], but only a few studies using methane as reductant have been performed [13].

As the main component of natural gas, methane is an attractive reductant of NO_x for a number of power sources [4,14,15]. However, the catalytic activation of methane usually implies elevated temperatures and products of its partial oxidation ($C_xH_yO_z$), which may act as intermediates in $DeNO_x$, are difficult to obtain with a reasonable yield. For this reason, methane is only poorly active towards the reduction of NO_x and its non-selective combustion into CO_2 and H_2O is usually promoted on noble metals in excess of oxygen. Another limitation for the development of CH_4-SCR catalysts is the weak general knowledge on the mechanisms involved in methane activation by NO_x. Both methane chemisorption and NO_x decomposition are structure-sensitive reactions and are

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* Corresponding author. Tel.: +33 387939106; fax: +33 387939101.
E-mail address: bazambre@univ-metz.fr (B. Azambre).

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supposed to be favoured on opened or rough surfaces [16]. Many studies consider that the rate-determining step in methane activation is the abstraction of the first hydrogen atom [17]. For instance, on the (1 0 0) surfaces of noble metals (Pd, Pt), methane has been shown to dissociate with a weak probability to give CH_3 and H adsorbed species. In presence of adsorbed oxygen, the probability to dissociate CH_4 is even more decreased due to the blocking of the active site or to a change of the metal electronic properties [17]. Yentekakis et al. have shown that the $CH_4 + NO$ reaction is a surface reaction between reaction intermediates that follows Langmuir-Hinshelwood kinetics [18]. At 420 °C, the maximal rate of N_2 formation on their Pd/YSZ catalyst was obtained for a $NO:CH_4$ ratio of 0.03. At higher ratios, the reaction is self-poisoned by the adsorbed oxygen left by the dissociation of NO [18].

In the present study, the reaction intermediates involved in CH_4-SCR and the factors controlling the reactivity of a Pd/ceria-zirconia catalyst are investigated using spectroscopic and gravimetric techniques under transient conditions.

2. Experimental

2.1. Catalyst preparation

The ceria-zirconia support ($Ce_{0.2}Zr_{0.8}O_2$, $S_{BET} = 180\ m^2/g$) was supplied by Rhodia and obtained from nitrate precursors. According to FT-Raman and XRD results [9,19], the $Ce_{0.2}Zr_{0.8}O_2$ sample has a predominantly tetragonal structure with inclusions of the m-ZrO_2 phase. The Pd-supported catalyst was prepared by incipient wetness impregnation of the ceria-zirconia mixed oxide using an appropriate amount of $PdCl_2$ precursor (99% pure product from Aldrich) dissolved in NH_3 in order to obtain a Pd loading of 1 wt%. After drying under vacuum at 70 °C, the catalyst was calcined under air at 500 °C during 2 h. The samples were labelled CZ28 for the $Ce_{0.2}Zr_{0.8}O_2$ support and Pd/CZ28 for the Pd-supported catalyst.

2.2. Characterizations and reactivity studies

First, the full temperature-programmed surface reaction (TPSR) was performed in a quartz reactor under the following conditions: 25–700 °C ($v = 10\,°C/min$); (1000 ppm CH_4/1000 ppm NO_2/balance He); GHSV = 4200 h^{-1}; $m_{catalyst} = 0.5$ g. Before the TPSR run, the catalyst was exposed to the gas mixture at room temperature for 2 h. A double detection system combining a gas cell (path length = 10 cm, 100 scans, resolution = 4 cm^{-1}) attached to the Biorad FTS185 FTIR spectrometer and a MS analyzer was used for the measurement of catalytic activities.

The nature of Pd oxidation states was investigated using DRIFTS of CO adsorption. Diffuse reflectance spectra were recorded in the 4000–700 cm^{-1} range (resolution 4 cm^{-1}, 100 scans) on a Bio-Rad FTS 185 spectrometer equipped with a MCT detector and the "Graseby Specac" optical accessory. Pure catalysts (i.e. without dilutent) were loaded into a Spectra-Tech environmental cell designed to work under controlled temperature and flowing gases. Prior to CO adsorption (2000 ppm/He, 100 mL/min), the samples were outgassed in situ under He up to 400 °C. Upon saturation by adsorbed CO, the gas phase was evacuated under He and the sample was heated up to 400 °C under He ($v = 10$ °C/min). In this series of experiment, the background reference is the single-beam spectrum of the catalyst pretreated at the same temperature before CO adsorption.

In order to assess the activity of the catalysts for methane combustion, additional TPSR experiments were carried out using methane alone. TPSR were performed using a CDS pyrolyzer coupled to a HP 5973 mass detector working in electron impact (EI) mode at 70 eV. In each experiment, 20 mg of samples were placed inside a quartz tube and heated from 25 up to 800 °C at a heating rate of 10 °C/min using CH_4 (2000 ppm/He) as the carrier gas. The individual m/z mass profiles corresponding to the range 2–100 amu were then monitored continuously during TPSR runs in order to check for the existence of reaction products.

In order to gain knowledge about the processes involved in CH_4 activation and the CH_4-SCR reaction, additional experiments were carried out using spectroscopic and thermogravimetric techniques under transient conditions. Whatever the technique used, the catalysts were pre-treated in situ under He at 400 °C before introduction of the reactive gases. The nature of reaction intermediates in the adsorbed form or in the gas phase was monitored by simultaneous in situ DRIFTS-MS analyses as a function of time at 400 °C under the following conditions: (i) sequential introductions of CH_4 (2000 ppm/He), NO_2 (2000 ppm/He) then CH_4 again (2000 ppm/He); (ii) exposure to the $CH_4 + NO_2$ mixture (1000/1000 ppm, balance He). During these experiments, mass spectroscopic data collected in the Selective Ion Monitoring (SIM) mode were recorded on a Balzers Thermostar Mass Spectrometer (EI mode-70 eV). Isothermal thermogravimetric studies at 300, 360 and 420 °C corresponding to the sequential exposure of the catalysts to CH_4 or NO_2 were performed using an Intelligent Gravimetric Analyzer (IGA) supplied by Hiden Analytical Ltd. The experimental conditions were close to those used for DRIFTS-MS experiments.

3. Results and discussion

3.1. TPSR under $CH_4 + NO_2$ (25–700 °C, $v = 10$ °C/min)

The $DeNO_x$ activity of the Pd/CZ28 catalyst and the CZ28 support were measured in temperature-programmed surface reaction mode from 25 to 700 °C. For the sake of clarity, only the TPSR profiles obtained for CH_4 and the sum of NO and NO_2 (total NO_x) are presented in Fig. 1. Below 280 °C, the TPSR profiles are dominated by the strong adsorption of NO_2 on the ceria-zirconia support, which explains that the total NO_x is under C_0 (1000 ppm). For the Pd/CZ28 catalyst, the measurement of NO_x concentrations well above C_0 between 350 and 480 °C indicates that desorption of surface nitrates is preponderant within this temperature range. Noteworthy, the occurrence of the desorption peak is delayed by about 40 °C for

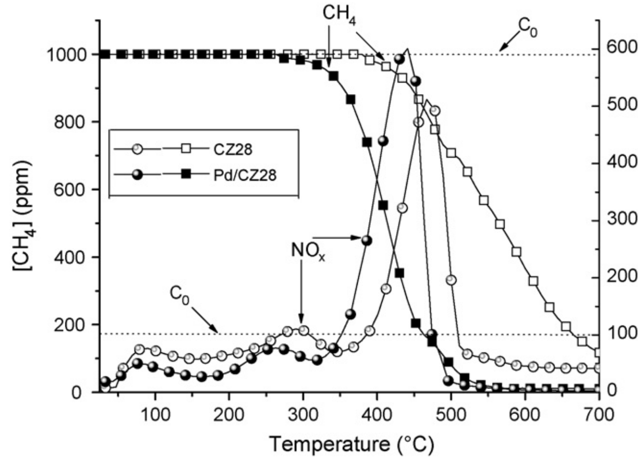

Fig. 1. TPSR profiles corresponding to the reaction of CZ28 and Pd/CZ28 in $CH_4 + NO_2$ (1000/1000 ppm/He) from 25 to 700 °C in absence of O_2 added ($\upsilon = 10$ °C/min) following 2 h adsorption at RT.

the CZ28 support. For both samples, methane consumption starts simultaneously with the onset of the NO_x desorption peak. On the support alone, methane conversion starts at 390 °C and remains always below 85% within the whole temperature range. By contrast, the CH_4-TPSR profile obtained for the Pd-supported catalyst displays some conversion already at 280 °C and nearly 100% conversion above 520 °C. For both the support and the catalyst, CO_2 was the major product obtained following methane consumption (not shown here). Meanwhile, measurable DeNO$_x$ activity is observed from 508 °C for CZ28 and 475 °C for Pd/CZ28, respectively. Here, the term DeNO$_x$ is used because N_2O was never observed during the TPSR reaction. Therefore, the obtaining of total NO_x concentrations below C_0 means probably that conversion to N_2 has occurred. Above 495 °C, DeNO$_x$ is almost total in presence of Pd whereas the best performance of the support alone is limited to 57% DeNO$_x$ in the 600–700 °C range.

It is worth noting that in presence of $NO + O_2$ (7%) in the feed instead of NO_2 (catalytic tests not shown here), the best performances achieved by the Pd/CZ28 catalyst for the CH_4-SCR reaction in the 25–500 °C range were only a 5% conversion to N_2 at 320 °C. The significance of these results is discussed in the next sections in agreement with characterization and reactivity studies.

3.2. DRIFTS study of CO adsorption

In order to have a better understanding of the oxidation states and reducibility of Pd species present after calcination on ceria-zirconia, an IR study of CO adsorption was performed. In Fig. 2 are reported the time-course DRIFTS spectra of adsorbed CO (1000 ppm/He) over the Pd/CZ28 catalyst at room temperature. From the analysis of the ν(CO) vibrations in the 2300–1800 cm^{-1} region, different CO adsorption sites can be evidenced on the support and catalyst. For the support, only very weak bands were observed at 2169 and 2110 cm^{-1} (not shown here). They may be assigned to CO coordinated on Ce^{4+} and Ce^{3+} cations, respectively [20,21]. By contrast, DRIFT spectra of the Pd/CZ28 catalyst (Fig. 2) display the sharp bands characterizing the presence of many kinds of CO adsorbed species. In agreement with the literature ([20] and references therein), the bands present after 2 min adsorption at 2145, 2105 and 2093 (shoulder) cm^{-1} can be attributed to CO linearly adsorbed on Pd^{2+}, Pd^{+} and Pd^{0}, respectively. The 2000–1900 cm^{-1} region is characteristic of CO bridged on two Pd sites. In this wavenumbers range, it is possible to find the 1992 cm^{-1} band tentatively assigned to $Pd_2^{+}(CO)$ and the 1930 cm^{-1} band corresponding to $Pd_2^{0}(CO)$ species [20]. The remaining band ca. 1880 cm^{-1} is probably due to CO bridged on three Pd atoms. By increasing the time of exposure to CO, the intensity of the band at 2145 cm^{-1} decreases at the expense of the 2093 and 1930 cm^{-1} bands. This shows that Pd^{2+} species were progressively reduced to the metallic state by CO during the experiment. Accounting for this process and the literature [19], it is believed that the palladium was initially present on CZ28 as isolated cations or very small PdO_x clusters.

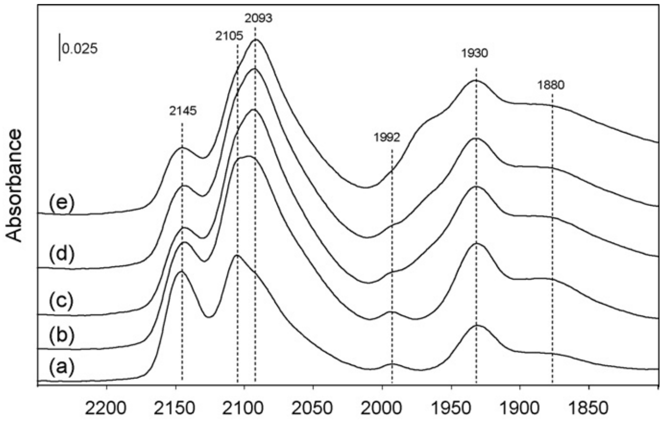

Fig. 2. DRIFTS spectra corresponding to the adsorption of CO at room temperature on Pd/CZ28 after: (a) 2 min; (b) 8 min; (c) 25 min; (d) 30 min; (e) 60 min.

3.3. TPSR experiments under CH_4 atmosphere

One of the problems associated to SCR with methane is the difficulty to use selectively CH_4 to reduce NO_x. In order to evaluate the importance of the methane combustion alone, a TPSR reaction was carried out in presence of CH_4 (2000 ppm). In Fig. 3(a–c), are shown the MS data corresponding to the evolution of CH_4 ($m/z = 15$), CO ($m/z = 28$) and CO_2 ($m/z = 44$) for the support and the Pd-supported catalyst. Other carbon-containing products, such as $C_xH_yO_z$ species, were not detected during these experiments. The emissions of CO_2 observed in the range 25–300 °C are only due to the contamination of the samples by adsorbed carbonates species, which is unavoidable for ceria and related materials. By comparing the support and the catalyst, it can be established that methane combustion on CZ28 remains rather weak in the whole range of temperatures studied, starting around 320 °C and becoming significant only beyond 600 °C. By contrast, the activity of Pd for the combustion of methane is clearly demonstrated. For Pd/CZ28, oxidation starts at 320 °C, and important emissions of CO_2 are

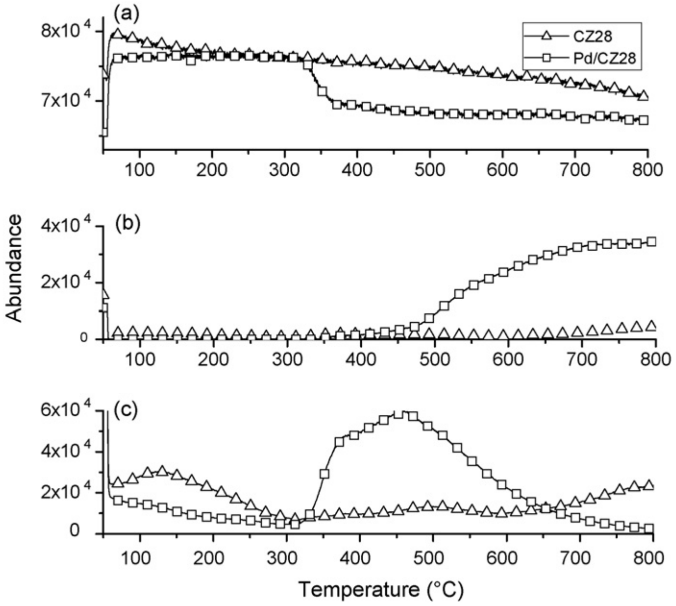

Fig. 3. TPSR in presence of CH_4 (2000 ppm/He) on CZ28 and Pd/CZ28: (a) *m*/*z* = 15 (CH_3^+); (b) *m*/*z* = 28 (CO^+); (c) *m*/*z* = 44 (CO_2^+). Heating program is 25 ≥ 800 °C (v = 10 °C/min).

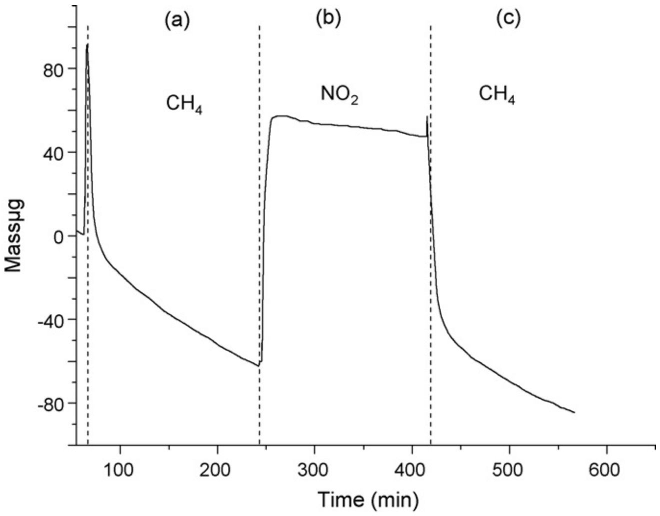

Fig. 4. Evolution of catalyst mass as a function of time when exposed to: (a) CH_4 (2000 ppm/He); (b) NO_2 (2000 ppm/He); (c) CH_4 (2000ppm/He) at 420 °C.

produced until awaiting a maximum at 450 °C. Beyond this temperature, there is a partial depletion of surface/lattice oxygens and the combustion becomes incomplete, CO being observed as the only product in the gas phase. Indeed, in absence of oxygen added to the feed, methane oxidation is only possible by reaction with surface oxygens, whose mobility increases with the temperature [19]. On the Pd/CZ28 catalyst, methane oxidation is somewhat maintained by spillover of surface/lattice oxygens from the support to Pd, the metal acting as a porthole. As oxygenated carbon species are produced, this process creates numerous oxygen vacancies in the vicinity of the metal and an overall reduction of the catalyst. In that respect, the colour change of the samples at the end of the experiment (green for the support and black for the Pd-supported catalyst) confirm that deep reduction occurs.

The above-mentioned results can be described by the following equations:

$$(\mathrm{Pd})\mathrm{Ce}_{0.2}\mathrm{Zr}_{0.8}\mathrm{O}_2 + x\mathrm{CH}_4 \Rightarrow (\mathrm{Pd})\mathrm{Ce}_{0.2}\mathrm{Zr}_{0.8}\mathrm{O}_{2-4x} + x\mathrm{CO}_2 + 2x\mathrm{H}_2\mathrm{O} \tag{1}$$

$$(\mathrm{Pd})\mathrm{Ce}_{0.2}\mathrm{Zr}_{0.8}\mathrm{O}_{2-4x} + y\mathrm{CH}_4 \Rightarrow (\mathrm{Pd})\mathrm{Ce}_{0.2}\mathrm{Zr}_{0.8}\mathrm{O}_{2-4x-y} + y\mathrm{CO} + 2y\mathrm{H}_2 \tag{2}$$

3.4. *Transient thermogravimetric studies*

Thermogravimetric analyses were carried out in transient conditions either at 300, 360 and 420 °C under CH_4 or NO_2 atmospheres in order to gain knowledge about the reaction mechanism involved in the SCR reaction in absence of O_2. Fig. 4 presents the evolution of the catalyst mass during sequential isothermal introductions of CH_4 (a), NO_2 (b) and CH_4 (c) at 420 °C. During the initial exposure to methane, a mass loss occurred. This means that the gasification of methane to CO_2(g) is preponderant over the production of adsorbed intermediates, e.g. $C_xH_yO_z$ or carbonates species, because in the latter case a mass gain would have been observed. Therefore, these results are consistent with those of the CH_4-TPSR reaction (Fig. 3). They signify that the mass loss is essentially caused by the removal of surface oxygens and that surface reduction occurs. As expected, a mass gain is observed after NO_2 introduction. In preliminary experiments [22], it was shown that NO_2 adsorbs on the surface of the support to form NO_2^-/NO_3^- adsorbed species, the bridged and chelated bidentate forms of nitrates being the more thermally stable (Fig. 4b). The subsequent mass loss observed during exposure of adsorbed NO_x species to CH_4 (Fig. 4c) is ascribed to a surface decomposition reaction leading presumably to the formation of N_2, N_2O and CO_2. Also, this means that RNO_x adsorbed intermediates, if formed, are not stable at this temperature. As the reaction temperature was decreased to 360 and 300 °C, rather similar TG profiles were obtained (not shown here), with however slight discrepancies. After the initial period of reduction by CH_4, the mass gain due to NO_x adsorption increased in the order $T_{300} > T_{360} > T_{420}$, as expected from the decreasing stability of nitrates in this range of temperatures. As shown by comparing the parts (b) and (c) of the TG curves, the mass loss observed upon exposure of the ad-NO_2 pre-covered catalyst surface to methane always equals approximately the mass gain observed during the exposure to NO_2. Despite the mass losses due to NO_x decomposition were more rapid at 360 and 420 °C than at 300 °C, these results show that the methane is able to reduce the ad-NO_x species in the 300–420 °C range. By comparing these results with those of the full TPSR reaction (Fig. 1), it can be stated that $DeNO_x$ probably starts at 280–300 °C (onset of CH_4 consumption) but is not directly visible on TPSR curves due the strong desorption of ad-NO_x species.

3.5. Transient DRIFTS-MS study

The nature of reaction intermediates present in the adsorbed state or in the gas phase were also monitored under transient conditions by DRIFTS-MS. Spectral data obtained during the sequential introductions of CH_4 and NO_2 are displayed in Fig. 5. When the catalyst is first exposed to methane at 400 °C, DRIFTS spectra display several bands at 1350 cm^{-1}, 1420 cm^{-1}, 1440 cm^{-1}, 1547 cm^{-1} and 1597 cm^{-1}, which increase during 25 min approximately (Fig. 5A1(a–c)). These absorptions are characteristic of carbonates and related species adsorbed on the surface [20,21]. Corresponding MS data (Fig. 5B1) indicate that the methane consumption during the ‘‘carbonates formation period’’ remained low. The ignition of

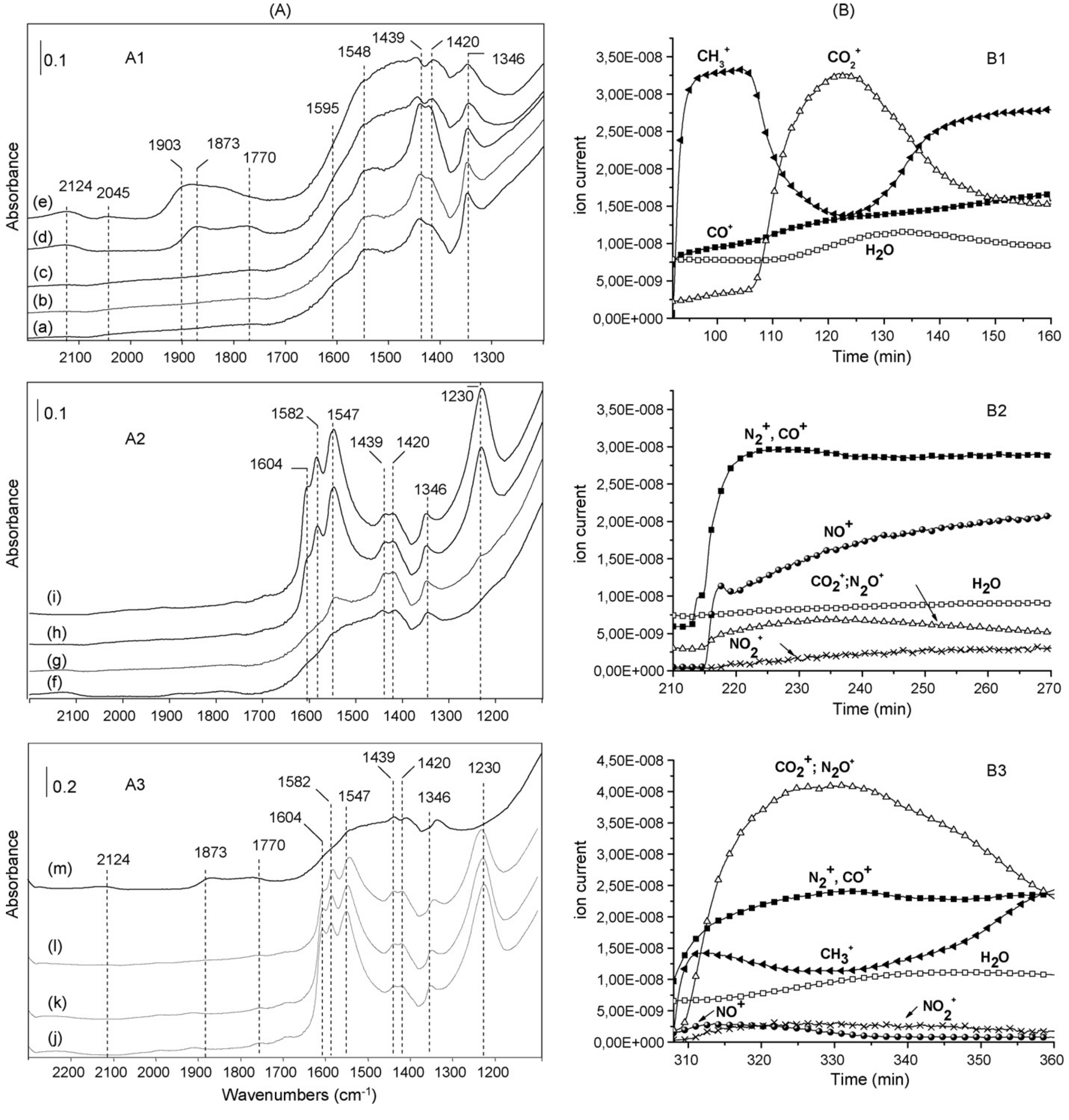

Fig. 5. Simultaneous DRIFT-MS data recorded during the sequential exposure of the Pd/CZ28 catalyst to CH_4 and NO_2 at 400 °C. A1: DRIFT data in the 2200–1200 cm^{-1} region corresponding to CH_4 (2000 ppm/He) introduction obtained after: (a) 5 min, (b) 10 min; (c) 25 min; (d) 35 min; (e) 65 min. A2: DRIFT data corresponding to NO_2 (2000ppm/He) introduction obtained after: (f) 3 min, (g) 10 min; (h) 22 min; (i) 29 min. A3: DRIFT data corresponding to CH_4 introduction obtained after: (j) 15 min, (k) 30 min; (l) 45 min; (m) 50 min. (B) MS data corresponding to sequence A.

the combustion reaction after 20–25 min is characterized by a strong decrease of the methane concentration and is accompanied by important emissions of CO_2 and H_2O (Fig. 5B1). Meanwhile, the IR spectrum changes drastically (Fig. 5A1(d and e)). Whereas the bands ca 1440–1420 cm^{-1} strongly decrease, new absorptions appear at 2120 cm^{-1}, 1870 cm^{-1} and 1774 cm^{-1}. The former band ca 2120 cm^{-1} could be assigned either to (Pd^+-CO) or to a $Ce^{4+} \rightarrow Ce^{3+}$ electronic transition due to surface or bulk reduction of the support [20,21]. The two latter bands are attributed to $(Pd^0)_2$-CO and $(Pd^0)_3$-CO, respectively (Fig. 5A1(d)) [23]. As CO is formed both in the adsorbed state (Fig. 5A1) and in the gas phase (Fig. 5B1), this shows again that, in agreement with CH_4-TPSR data, depletion of the reactive oxygens needed for the total combustion occurs. Moreover, the concomitant partial reduction of some Pd sites is observed here by DRIFTS, under in situ conditions. DRIFTS spectra obtained after 65 min of exposure to CH_4, display a new band at 2045 cm^{-1} corresponding to linearly adsorbed CO on Pd metallic clusters interacting with oxygen vacancies. Also, the intensity of the bands at 1870 cm^{-1} and 1820 cm^{-1} increase, while the band at 1774 cm^{-1} decreases.

As the reduced catalyst surface is exposed to NO_2, the bands corresponding to adsorbed CO quickly disappear (Fig. 5A2(a and b)) while some N_2 (N_2O and CO_2) are simultaneously detected by MS (Fig. 5B2). It can be therefore concluded that some $DeNO_x$ occurred on the reduced catalyst surface. After 10 min, new bands corresponding to adsorbed NO_3^- species are detected at 1604 cm^{-1}, 1582 cm^{-1}, 1547 cm^{-1}. Meanwhile, the pair of bands at 1439–1420 cm^{-1} characteristic of carbonates and related species re-appear due to oxygen transfer from NO_2 to $Pd^0(CO)_x$ species (Fig. 5A2(b–d)) [22,24]. At increasing exposure times to NO_2, the concentrations of NO_2^+ and NO^+ fragments increase as the surface becomes progressively re-oxidized and is less active for $DeNO_x$.

During the second CH_4 introduction on the ad-NO_x pre-covered catalyst surface, nitrite/nitrate bands decrease due to the reaction between methane and ad-NO_x species, showing again that $DeNO_x$ occurs at this temperature (Fig. 5A3(a–c)). After 50 min of exposure to methane, all the bands attributed to NO_x ad-species have disappeared, and the DRIFT spectra characteristic of CH_4 adsorbed on the reduced surface is recovered (Fig. 5A3(d) and Fig. 5A1(d and e)). Simultaneously, an important consumption of methane added to the evolution of N_2, N_2O and CO_2 are observed in the gas phase (Fig. 5B3). By comparing the CH_4 profiles on Fig. 5B1 and B3, it can be established that the consumption of methane is considerably more important in presence of ad-NO_x species and occurs without any induction period.

4. Conclusions

In this study, we aimed to investigate the roles of palladium and ceria-zirconia support in the SCR of NO_x by methane both in absence and presence of excess oxygen.

By DRIFTS of adsorbed CO, it was shown that palladium is initially present in the calcined $Pd/Ce_{0.2}Zr_{0.8}O_2$ catalyst as Pd^{x+} ionic species surrounded by surface oxygens or small PdO_x clusters exhibiting high reducibility.

TPSR profiles obtained under $CH_4 + NO_2$ atmosphere in absence of added oxygen clearly demonstrated the beneficial role of Pd in the activation of methane by NO_x. For the $Pd/Ce_{0.2}Zr_{0.8}O_2$ catalyst, the onset of methane consumption started at 280 °C (410 °C for the support alone) and almost 100% NO_2 conversion to N_2 was reached above 500 °C.

By contrast, the poor performances (5% $DeNO_x$ at 320 °C) of the $Pd/Ce_{0.2}Zr_{0.8}O_2$ catalyst for CH_4-SCR in presence of excess O_2 were due to the high activity of palladium for the non-selective oxidation of methane to CO_2. The methane combustion reaction, which becomes competitive to $DeNO_x$ above 320 °C, is promoted on $Pd/Ce_{0.2}Zr_{0.8}O_2$ by the strong interplay between the active phase and the labile surface oxygens of the reducible support. In presence of O_2 in the feed, the oxygen vacancies generated by reduction with CH_4 are easily replenished and the palladium is maintained in an oxidized PdO_x state. In absence of excess O_2, the role of the ceria-zirconia as an oxygen buffer for the combustion reaction is somewhat limited and total NO_x decomposition took place when the catalyst had been extensively reduced and/or surface had reconstructed.

As shown by transient DRIFT-MS and TGA analyses, the SCR mechanism may involve a surface reaction between some adsorbed CO_x species generated by CH_4 activation on reduced Pd^+ or Pd^0 sites (interacting with oxygen vacancies) and nitrates/nitrites adsorbed on ceria-zirconia.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2007.12.136.

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