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Campa, Maria Cristina, Fierro, Giuseppe, Doyle, Aidan M , Tuti, Simonetta, Catracchia, Carlotta and Pietrogiacomini, Daniela (2023) Combined use of in situ and operando-FTIR, TPR and FESEM techniques to investigate the surface species along the simultaneous abatement of N<sub>2</sub>O and NO on Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts. *Surfaces and Interfaces*, 42. 103502 ISSN 2468-0230

**DOI:** <https://doi.org/10.1016/j.surfin.2023.103502>

**Publisher:** Elsevier

**Version:** Published Version

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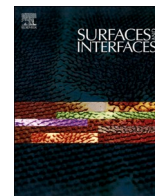
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# Combined use of *in situ* and *operando*-FTIR, TPR and FESEM techniques to investigate the surface species along the simultaneous abatement of N<sub>2</sub>O and NO on Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts

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## ARTICLE INFO

### Keywords:

NO<sub>x</sub> and N<sub>2</sub>O simultaneous abatement with CH<sub>4</sub>  
Pt,Pd,Rh on TiO<sub>2</sub>-ZrO<sub>2</sub>  
Pt,Pd,Rh on TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub>  
SCR reactions  
TPR analysis  
*in situ* FTIR characterisation  
*operando*-FTIR analysis

## ABSTRACT

Pt,Pd,Rh supported on TiO<sub>2</sub>-ZrO<sub>2</sub> and TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> show a promising catalytic behavior for the simultaneous selective catalytic reduction of NO and N<sub>2</sub>O with CH<sub>4</sub> in the presence of O<sub>2</sub> (SCR<sub>sim</sub>). The nature of the catalytic species and the formation of intermediate species on the catalyst surface were investigated by combining several techniques. The co-existence of fully and partly reduced noble metals are strictly dependent on the O<sub>2</sub>/CH<sub>4</sub> ratio in the feed which is crucial for a good catalytic activity. When the O<sub>2</sub>/CH<sub>4</sub> ratio is less than 1, NO and N<sub>2</sub>O were efficiently and simultaneously reduced with negligible formation of by-products. As the O<sub>2</sub>/CH<sub>4</sub> ratio was higher than 1, CH<sub>4</sub> combustion prevailed. The CeO<sub>2</sub> made the catalyst slightly more efficient, likely improving the solid redox properties at the interface between noble metal particles and gaseous reactants. The *operando* FT-IR analysis identified some surface intermediate species involved in the reaction pathways. In the presence of NO, surface nitrite/nitrate species that are strongly adsorbed on the catalysts surface competed with the N<sub>2</sub>O adsorption sites. An assay of the SCR<sub>sim</sub> catalytic behaviour in the presence of water revealed that the catalyst with ceria has a good catalytic activity and stability along tests simulating nearly real conditions.

## 1. Introduction

The catalytic abatement of nitrogen oxides, i.e. NO<sub>x</sub> and N<sub>2</sub>O, to less harmful species has been studied for decades and continues to be a topic of research in the pursuit of new and improved systems for emissions abatement [1]. These compounds are by-products of a number of processes e.g. transportation, energy production and bulk chemicals synthesis (nitric acid and adipic acid) and are problematic due to their toxicity (NO) and greenhouse gas potency (N<sub>2</sub>O) [2]. It follows that it is of great relevance to develop catalysts which are able to abate simultaneously NO and N<sub>2</sub>O. Most studies have focussed on Selective Catalytic Reduction (SCR) of NO, which successfully transforms NO<sub>x</sub> to N<sub>2</sub>, by reaction with suitable reagents e.g. CH<sub>4</sub>, CO, H<sub>2</sub>, or NH<sub>3</sub> [3,4]. The most common active components in Three-Way-Converters (TWC)

continue to be noble metals, whereby Pt and Pd are active for hydrocarbon oxidation and Rh for NO<sub>x</sub> reduction [5–9]. Recently there has been a greater emphasis on N<sub>2</sub>O due to its environmental importance and presence in exhaust streams [2,10]. The SCR of NO and the SCR of N<sub>2</sub>O has been extensively reported individually, despite the existence of both compounds in exhaust streams. When both gases are present, as in the industrial nitric acid plants, the EnviNOx® process [11] is effective for the abatement of NO<sub>x</sub> and N<sub>2</sub>O by SCR over two catalytic beds of Fe-zeolite where NO<sub>x</sub> is abated by NH<sub>3</sub> and N<sub>2</sub>O by CH<sub>x</sub> or by NO-assisted decomposition [12,13]. In other studies NO and N<sub>2</sub>O were removed sequentially by SCR over Pd-modified perovskites [14] or over dual-bed reactors consisting of Co-ZSM-5 and Pd/Fe-ZSM-5 [15] or In/Al<sub>2</sub>O<sub>3</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> [16]. In contrast, the simultaneous SCR of NO and N<sub>2</sub>O is sparsely discussed in the literature. Some studies were made

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<https://doi.org/10.1016/j.surfin.2023.103502>

Received 14 July 2023; Received in revised form 5 October 2023; Accepted 7 October 2023

Available online 9 October 2023

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over Ag/ZSM-5 [17], Fe-zeolite catalysts [18–22] and over a commercial Bi-Ni-oxide modified  $V_2O_5$ - $MoO_3$ / $TiO_2$  catalyst [23]. We have reported the simultaneous abatement of NO and  $N_2O$  in the presence of  $O_2$  with  $C_3H_6$  over  $ZrO_2$  supported  $CoO_x$  and  $FeO_x$  [24] and over Fe-, Co- and Ni-exchanged MOR catalysts with  $CH_4$  [25], proposing also a reaction pathway using *operando*-FTIR [26].

There is a tendency in the exploration of heterogeneous catalysts to study one catalyst and one reaction in a given experiment. This method is entirely appropriate to infer a correlation between catalyst structure and reactivity, and has brought about a step change in our understanding of catalysis. Of course, ‘real’ catalysts, e.g. those employed in a TWC washcoat, must be active for a number of different reactions simultaneously and, therefore, require a mixture of supports and catalytically active metals. This adds complexity from (a) the presence of a plurality of catalysts, each of which provides unique catalytic properties analogous to those in their distinct forms, (b) the occurrence of synergistic effects that diverge from those of individual catalysts and (c) the coexistence of several competing reactants each of which interacts differently with the catalysts. This approach of using different mixed supports/catalysts generated promising results in the simultaneous abatement of NO and  $N_2O$  with  $CH_4$  as reductant over Pt,Pd,Rh/ $Al_2O_3$ - $SiO_2$  and Pt,Pd,Rh/ $Al_2O_3$ - $ZrO_2$  [27] and has motivated us to continue the study further.  $CH_4$  is an appealing reductant due to a cheap and plentiful supply of natural gas (predominantly  $CH_4$ ) and being increasingly used as a low carbon substitute for diesel in dual fuel engines for heavy good vehicles (HGVs) [5]. In this work, the activity and selectivity of Pt,Pd,Rh/ $TiO_2$ - $ZrO_2$  and Pt,Pd,Rh/ $TiO_2$ - $ZrO_2$ - $CeO_2$  catalysts in the simultaneous selective catalytic reduction,  $SCR_{sim}$ , of NO and  $N_2O$  with  $CH_4$  were investigated. Different  $O_2$  feed contents were used as the extent of SCR is dependent on the choice of either lean or rich conditions in the feed [28].

In order to get more insight into the complex mechanism of the  $SCR_{sim}$  reaction, the SCR with the single reactant ( $SCR_{NO}$ ,  $SCR_{N_2O}$ ), as well as the Catalytic Reductions in the absence of  $O_2$  ( $CR_{sim}$ ,  $CR_{NO}$ ,  $CR_{N_2O}$ ) were also investigated. For the same purpose, we studied the  $N_2O$  decomposition by itself or in the presence of  $O_2$  and NO, and the  $CH_4$  combustion reaction as well.

A combined use of several techniques (XRD,  $N_2$  physisorption, FESEM and  $H_2$ -TPR) provided a more comprehensive view of the catalyst characteristics. In order to investigate the surface aspects in more detail, the FTIR spectroscopy has been used. In particular, the interaction of probe molecules (NO or CO) with the catalyst surface under a controlled atmosphere (i.e. *in situ*) was studied by *in situ* FTIR technique. Moreover, the formation of surface intermediates under working condition was investigated by *operando*-FTIR (i.e. spectroscopic measurements carried out in a catalytic reactor in the presence of the reactants mixture and in the reaction temperature range while the catalyst performance is evaluated on-line).

A cross-analysis of the catalytic data with the *operando*-FTIR findings provided new insight into the pathways of the  $SCR_{sim}$ , shedding more light on the very complex mechanism of this reaction.

Finally, in order to provide just a first sight of the catalytic behaviour under nearly real conditions, an assay of the catalytic activity was made in the presence of water.

## 2. Experimental

### 2.1. Catalysts preparation

Catalysts were prepared by ion-exchange using identical quantities of Pt, Pd and Rh and catalyst treatment (i.e. ultrasound, stirring, filtering, washing, drying and calcination) to that reported previously [27]. The supports were prepared by mixing 1.0 g of  $TiO_2$  (anatase, Millenium) with 1.0 g of  $ZrO_2$  (monoclinic, Sigma 99%) for both the Pt, Pd,Rh/ $TiO_2$ - $ZrO_2$  and Pt,Pd,Rh/ $TiO_2$ - $ZrO_2$ - $CeO_2$  catalysts, in this last preparation being added 0.2 g of  $CeO_2$  (Sigma Aldrich, 99%). The

solutions, previously prepared, containing the three noble metals (Pt, Pd, Rh) were added to each of these two supports batches. The resulting suspensions were subjected to ultrasonic treatment, washed, dried and calcined for 4 h in air at 550°C thus giving the final Pt,Pd,Rh/ $TiO_2$ - $ZrO_2$  and Pt,Pd,Rh/ $TiO_2$ - $ZrO_2$ - $CeO_2$  catalysts.

### 2.2. Catalyst characterization

#### 2.2.1. Chemical, structural and morphological analysis

The quantitative analysis of noble metals was performed by the Wet Chemistry (Te-collection)-ICP-OES methodology in the laboratory of BASF Italia S.p.A., Rome. According to this procedure, the sample is first fused with sodium peroxide, then the melt was dissolved in hot de-ionized water and acidified with hydrochloric acid until all salts were dissolved. At this point, a solution of tellurium chloride was added, followed by the addition of a solution of stannous chloride with a consequent quantitative coprecipitation of Pd, Pt and Rh. Finally, the tellurium precipitate containing the noble metals was dissolved in aqua regia and the Pd, Pt and Rh measured by ICP-OES.

A Philips PW 1729 diffractometer was used to obtain the X-Ray Diffraction (XRD) patterns under the following experimental conditions: X-ray tube operating at 40 kV and 20 mA, Cu K $\alpha$  (Ni-filtered) radiation ( $\lambda = 1.5406 \text{ \AA}$ ),  $10$ – $70^\circ$   $2\theta$  range (step size  $0.02^\circ$ ; step time 1.25 s).

A Micromeritics ASAP 2020 was used for obtaining BET surface areas through nitrogen adsorption/desorption measurements (relative pressure range 0.05–0.30) at  $-196^\circ\text{C}$ . Prior to analysis, samples were degassed under vacuum ( $p < 10^{-3}$  Pa) for 12 h at  $300^\circ\text{C}$ .

A Field-Emission Scanning Electron Microscope (FESEM) was used to study the morphology of the catalysts either as fresh sample or after catalysis by using an AURIGA Zeiss 405 HR-FESEM instrument which was equipped with an Energy Dispersive X-ray (EDX) Spectroscopy Bruker apparatus for elemental detection.

#### 2.2.2. TPR experiments

The reducibility of the two catalysts was investigated by temperature-programmed reduction (TPR) with  $H_2$  over either the fresh, i.e. as prepared, samples (TPR<sub>fresh</sub>) or after they underwent catalytic tests (TPR<sub>catal</sub>). The TPR experiments were carried out with a Thermo Scientific TPDRO1100 apparatus provided with an in-flow system. The consumption of  $H_2$  was measured with a hot wire detector (HWD) calibrated through the reduction of a weighted mass of CuO (purity 99.99% Sigma Aldrich). The catalyst as powder was introduced into a fixed bed tubular reactor in quartz which was placed inside a cylindrical oven whose temperature is regulated by a temperature controller program. At the exit of the reactor, a soda-lime trap was used to remove water formed in the reaction during reduction.

Before starting a TPR run, a weighted amount of a fresh catalyst (0.050–0.100 g) was pretreated at  $500^\circ\text{C}$  *in situ* under flowing oxygen (10%  $O_2/He$ , v/v) and left at this temperature for 5 min. Then the sample was cooled to room temperature in Ar before starting a TPR run. A mixture of  $H_2/Ar$  (5% v/v,  $30 \text{ ml min}^{-1}$ ) passed through the sample and the temperature raised from RT up to  $500^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$ , keeping such a final temperature for 1 h. Such experimental operating variables were chosen in order to avoid artefacts along the TPR experiments [29]. The TPR analysis of the catalysts after catalytic tests was made using the same pretreatment *in situ* under flowing oxygen and under the same experimental conditions as for the analogous experiments on the fresh catalysts.

#### 2.2.3. In situ FTIR and operando-FTIR measurements

A Perkin Elmer Frontier spectrometer, equipped with an MCT detector, was used to record FTIR spectra at a resolution of  $4 \text{ cm}^{-1}$ . The fresh catalysts as powder (20 mg) were pressed ( $2 \times 10^4 \text{ kg cm}^{-2}$ ) to obtain self-supporting wafers of about  $10 \text{ mg cm}^{-2}$ .

The *in situ* characterization was carried out by the adsorption of probe molecules (CO or NO) on samples activated before the

experiments, i.e. (i) evacuation from RT to 500°C, (ii) heating in O<sub>2</sub> at 500°C for 1 h and, in the end, (iii) outgassing at the same temperature for 1 h. For these measurements, a quartz cell provided with KBr windows was used allowing thermal treatments in vacuum or in a controlled atmosphere.

In the *operando*-FTIR experiments, a stainless-steel IR reactor, provided with CaF<sub>2</sub> windows, was used to record spectra on sample wafers up to 500°C under gas stream. The reactor was connected to the same flow apparatus used for catalytic measurements equipped with a gas-chromatograph apparatus for the online analysis of reactants and products. Before the experiments, samples were activated at 500°C in a feed of a 2.5% O<sub>2</sub>/He (v/v) mixture and then kept at this temperature for 90 min. Then they were cooled from 500°C to the desired temperature under He flow before being exposed to the catalysis-like feeding mixtures. Spectra were recorded at increasing steps of temperature (from 200 to 500°C). It should be noted that the *operando*-FTIR spectra reported in the figures are difference spectra obtained from the subtraction of the spectra recorded exposing samples to the catalysis-like reactant stream at a given temperature and the spectra coming from a purposely-arranged blank experiment in which the sample was exposed to a He stream at the same temperature.

### 2.3. Catalytic tests

A flow apparatus at atmospheric pressure was used for the catalytic activity measurements in steady state conditions. The feeding mixtures were obtained by mixing gas flows (pure He, 3% NO in He, 3% N<sub>2</sub>O in He, 1.5% CH<sub>4</sub> in He and 10% O<sub>2</sub> in He, all purchased from RIVOIRA and used without further purification) that were independently regulated by mass flow controller-meters (MKS Instruments). In order to guarantee the maximum stream homogeneity, the gas flows were mixed in a glass ampoule before entering the reactor. The catalysts, as powder (ca. 0.150 g), were placed on a sintered frit of a quartz reactor. The analysis of reactants and products was made by a gas-chromatograph (Agilent 7890A GC system) equipped with three columns (Molsieve 5A, for detecting O<sub>2</sub>, N<sub>2</sub> and CO; Porapack Q for detecting CO<sub>2</sub> and N<sub>2</sub>O; Na<sub>2</sub>SO<sub>4</sub>-doped alumina for detecting CH<sub>4</sub>) and two detectors (TCD and FID). NO was detected by Molsieve 5A only in the absence of O<sub>2</sub> in the reactant stream as the NO<sub>2</sub> formed in the presence of O<sub>2</sub> is not detectable by GC systems. For all the reactants (N<sub>2</sub>O, NO, O<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>) the GC detection sensitivity is about 10 ppm, with the exception of CH<sub>4</sub> whose detection limit is about 1 ppm.

Before any catalytic run, catalysts were activated by feeding 2.5% O<sub>2</sub>/He (v/v) mixture (100 cm<sup>3</sup> min<sup>-1</sup>) from RT to 500°C and then keeping them isothermally at 500°C for 90 min. In the catalytic runs, the temperature was changed in a random sequence maintaining a constant temperature for at least 30 min (along which three consecutive GC analyses were made to be sure that data did not change) while the catalytic stream continued to flow over the catalyst (total flow rate = 100 cm<sup>3</sup> STP/min and GHSV = 40000 NL kg<sup>-1</sup> h<sup>-1</sup>). For the sake of comparison, the reactant concentrations, i.e. N<sub>2</sub>O (4000 ppm), NO (4000 ppm), CH<sub>4</sub> (4000 ppm) and O<sub>2</sub> (20000, 5000 or 2500 ppm) (v/v, He as balance), were kept the same in all the reactions investigated. For the catalytic

tests in presence of water, a wet feed containing 2.5% v/v of H<sub>2</sub>O was obtained using a saturator by bubbling a He stream in the H<sub>2</sub>O liquid phase kept at constant temperature (44°C).

Conversions obtained at various W/F ratios (W=sample weight, F=flow rate) indicated that, in our conditions, the reaction is under kinetic control without diffusion effects.

As in detail reported elsewhere [27], percent N<sub>2</sub>O, CH<sub>4</sub>, total NO or O<sub>2</sub> conversion was calculated as 100 × (molecules consumed)/(molecules injected). Percent NO conversion to N<sub>2</sub> was calculated in SCR<sub>NO</sub> as 200 × (N<sub>2</sub> produced)/(NO injected) and in SCR<sub>sim</sub> as 200 × (N<sub>2</sub> produced – N<sub>2</sub>O consumed)/(NO injected). Percent CO<sub>2</sub> selectivity was calculated as 100 × (CO<sub>2</sub> formed)/(CO<sub>2</sub>+CO molecules formed). The N<sub>2</sub>O/CH<sub>4</sub> and O<sub>2</sub>/CH<sub>4</sub> ratios were calculated as (N<sub>2</sub>O, or O<sub>2</sub>, molecules consumed)/(CH<sub>4</sub> molecules consumed).

The C-balance was calculated as (total C atoms inlet)/(total C atoms outlet). The N-balance was calculated as (total N atoms inlet)/(total N atoms outlet). When NO and O<sub>2</sub> are simultaneously present in the mixture, N-balance cannot be calculated as undetectable NO<sub>2</sub> is also formed.

## 3. Results and discussion

### 3.1. Catalyst characterization

The analytical content (wt%) of Pt, Pd, and Rh and the BET specific surface areas of the Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts are reported in Table 1. The specific surface areas of the catalysts correspond well to the mean value of the sum of the surface areas of the two mixed supports.

The XRD patterns of the fresh catalysts shows only the reflections of the anatase TiO<sub>2</sub>, monoclinic ZrO<sub>2</sub> and CeO<sub>2</sub> supports (Fig. 1), whose XRD patterns are matching those reported in the reference JCPDS cards (21–1272 for TiO<sub>2</sub> anatase, 37–1484 for monoclinic ZrO<sub>2</sub> and 34–394 for CeO<sub>2</sub>). In both fresh catalysts, within sensitivity limits of the technique, no peaks belonging to Pt, Pd and Rh oxide species are detected, suggesting that the diameter of noble metal oxide crystallites, as a mean value, is below ca. 5 nm.

The XRD patterns of both catalysts after catalysis are very similar to those of the fresh materials, but in the case of Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> a very small and broad peak appears at 2θ=40.2° (Fig. 1b) which corresponds to the most intense peak of the Pd metal (Pd(111) [JCPDS card 5-0681]), being the most intense diffraction peak of Pt and Rh metals in different position (39.9° for Pt(111) [JCPDS card 4-0802], and 41.2° for Rh(111) [JCPDS card 5-0685]). Moreover, from the linewidth analysis by using the Scherrer equation, an average crystallite size of Pd of ca. 20 nm is calculated, indicating that some Pd metal crystallites are formed under the catalytic runs.

For the catalysts after catalysis both the line positions and the linewidths of the supports are nearly identical to those for the fresh catalysts, suggesting that, besides the formation of Pd metal phase, no remarkable macroscopic, structural or morphological changes occur in the solid resulting from the catalytic runs.

In the FESEM images and corresponding EDX elemental maps of the

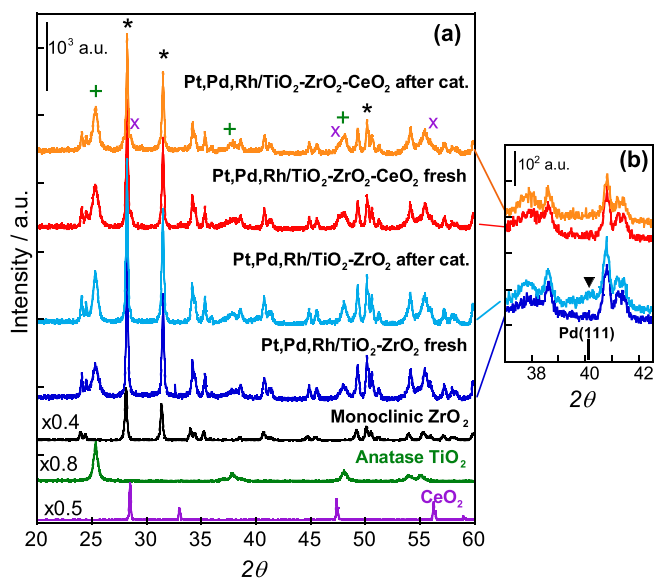
**Table 1**  
Pt, Pd and Rh content, specific surface areas and TPR quantitative analysis.

Sample Name	Pd wt%	Pt wt%	Rh wt%	S <sub>BET</sub> <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	H <sub>2</sub> uptake (mmol g <sup>-1</sup> )		
					theor. <sup>b</sup>	exper. (fresh catalyst)	exper. (after catalysis)
TiO <sub>2</sub>				103			
ZrO <sub>2</sub>				35			
Pt,Pd,Rh/TiO <sub>2</sub> -ZrO <sub>2</sub>	0.66	0.85	0.82	49	0.22	0.20	0.14
Pt,Pd,Rh/TiO <sub>2</sub> -ZrO <sub>2</sub> -CeO <sub>2</sub>	0.65	0.84	0.98	64	0.25	0.23	0.18

<sup>a</sup> S<sub>BET</sub> = BET specific surface areas (m<sup>2</sup> g<sup>-1</sup>)

<sup>b</sup> The theoretical H<sub>2</sub> consumption was calculated under the hypothesis that PdO, PtO and Rh<sub>2</sub>O<sub>3</sub> were the oxide-like species formed after calcination at 500°C





**Fig. 1.** XRD patterns of Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts as fresh samples or after catalysis (section a). The XRD patterns of monoclinic ZrO<sub>2</sub> (\*), anatase TiO<sub>2</sub> (+), and CeO<sub>2</sub> (x) supports are also reported as reference. The marks on the XRD patterns of the catalysts refer to the position of the three most intense lines of the supports. Section b shows the magnification of the region in which the most intense peak of Pt, Pd, Rh metal phases are expected, showing the Pd(111) reflection position. From the FWHM value of the Pd peak, the Pd mean crystallite diameter (reported in the text) was calculated by the Scherrer equation ( $d = K\lambda/\beta\cos\theta$ ).

Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> as fresh catalysts (Fig. 2a), titania particles (pink coloured) can be distinguished, being characterized by a rougher surface, whereas particles with a more uniform surface correspond to zirconia (green coloured). The CeO<sub>2</sub> support, although not visible in the images due to its very low amount, can be identified in the EDX elemental maps (see Fig. 2a). The noble metal oxides, detected by EDX, were not distinguished in the FESEM images, probably because they are dispersed on the support as very small nanoparticles, this being supported also by XRD analysis which did not reveal any noble metal oxides phases.

In the catalysts after catalysis (Fig. 2b), if compared to the fresh material, the FESEM images show noble metal nanoparticles which are heterogeneous in size (from ca. 2 to ca. 50 nm), lying on the supports and characterised by rounded morphology. These noble metal nanoparticles are made by aggregates of small crystallite, which only in the case of Pd in Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> catalyst are detected by XRD (vide supra), which is able to reveal crystallites larger than ca. 5 nm. In the EDX elemental maps of such crystallite aggregates, the Pd, Pt and Rh escaped the detection as single particles, showing signals for each noble metal spread all over the scanned area (insets in Fig. 2b).

After catalysis in the presence of H<sub>2</sub>O (Fig. 2c), a larger heterogeneity in size of noble metal nanoparticles is observed and a detectable aggregation of Pd occurred. Indeed, Pd metal is now distinguished by EDX analysis in the form of aggregates reaching ca. 100 nm in size (see Fig. 2c, inset EDX analysis), suggesting that Pd is more sensitive with respect to Pt and Rh to be aggregated in the presence of H<sub>2</sub>O.

### 3.2. TPR analysis

The H<sub>2</sub>-TPR profiles of the fresh Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts are both characterized by a rather complex pattern which, with some differences, is still present in the reduction profiles of the catalysts after the catalytic runs (Fig. 3a and b).

The common features evident in the TPR profiles of both catalysts

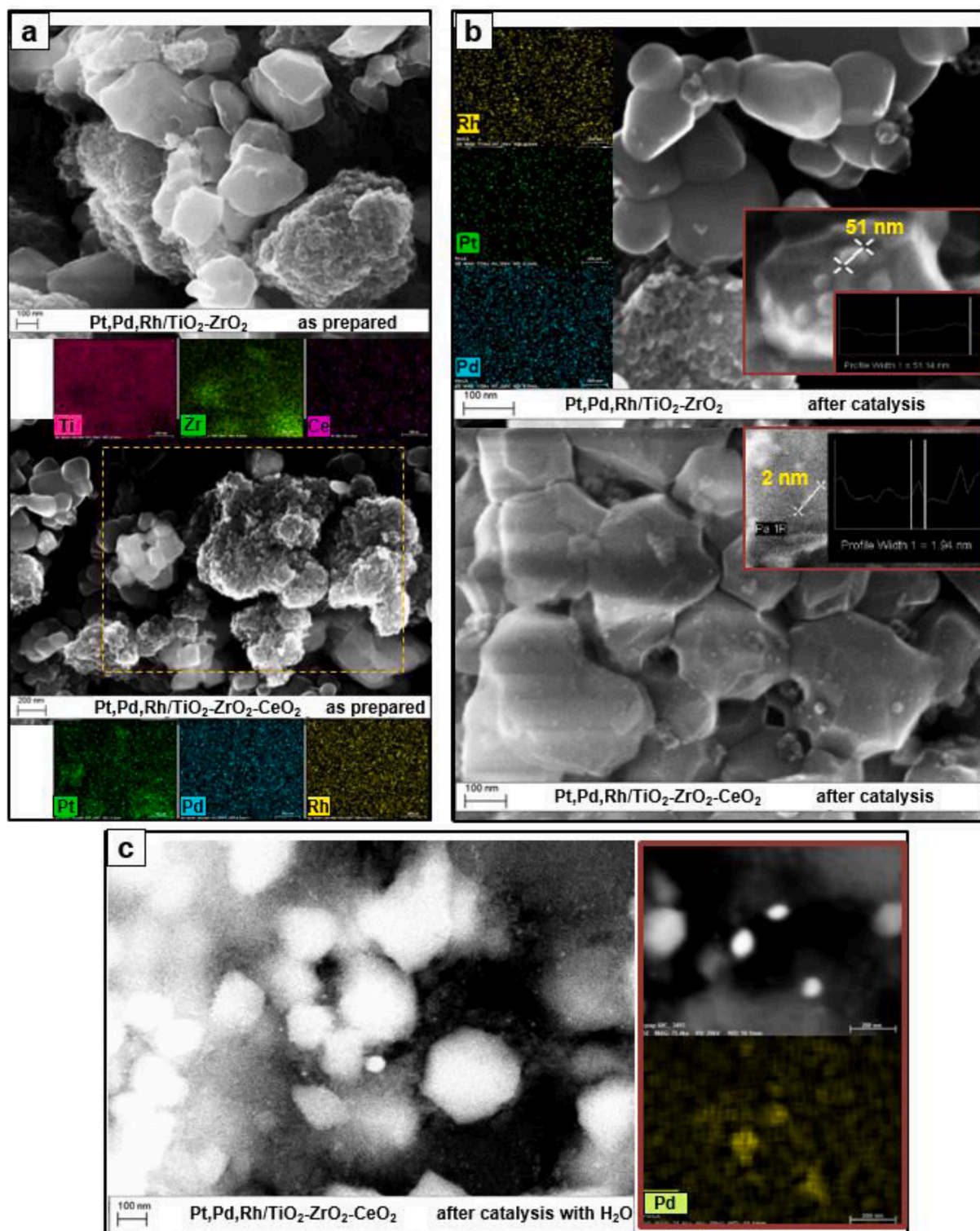
either as fresh materials or after catalysis are represented by a wide band whose intensity, as a whole, is continuously increasing with increasing temperature (see Fig. 3). In such a wide band some peaks can be distinguished, less resolved in the lower temperature side (from RT up to about 280°C), with the exception of the Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalyst in which after catalysis the poor resolved peaks became more evident (see Fig. 3b). For both catalysts, regardless their initial state (fresh or after catalysis), a well-defined and larger peak appeared in the high temperature side (from 280 to 500°C). Such a complex shape can be due to the gradual occurring of the reduction of the PdO<sub>x</sub>, PtO<sub>x</sub> and Rh<sub>x</sub>O<sub>y</sub> oxide-like species as well as to possible overlapping of these reduction processes. A further complication is represented by two other factors: (i) the influence of the supports, in particular CeO<sub>2</sub>, that very likely play a role in these processes through a noble metal oxide-support interaction, or a synergy between CeO<sub>2</sub>, ZrO<sub>2</sub> and TiO<sub>2</sub> as recently reported in literature [30]; (ii) the formation of metals (Pd and Pt in the first stage) which, as it is well known, can activate the H<sub>2</sub> molecule thus enhancing the overall reduction process.

For both the Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts, a negative peak at ca. 70°C can be attributed to the decomposition of some Pd-hydride species ( $\beta$ -PdH<sub>x</sub>) which can give rise to the desorption of H<sub>2</sub> (thus enriching the reducing stream) chemisorbed on the Pd surface or adsorbed in the bulk of metal Pd particles [31–33]. In agreement with a mechanism already described [31], it can be suggested that PdO<sub>x</sub>-like species, formed after calcination at 550°C on the TiO<sub>2</sub>-ZrO<sub>2</sub> and TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> supports, are reacting first with H<sub>2</sub> even at room temperature forming  $\beta$ -PdH<sub>x</sub> species. Interestingly, such a negative peak is always present regardless of the catalyst composition and its initial state (fresh or after catalysis), suggesting that the formation of  $\beta$ -PdH<sub>x</sub> species at low temperature is not influenced by the catalyst history.

In the lower temperature region (from 50 up to ca. 180°C), besides the negative peak, a wide band characterized by poorly resolved components can be observed which, as a whole, can be due to the reduction of isolated or well dispersed PdO<sub>x</sub>, PtO<sub>x</sub> and Rh<sub>x</sub>O<sub>y</sub> species [31,34,35].

In the middle temperature region (from ca. 180°C up to ca. 265°C), the H<sub>2</sub> detector signal is still slowly increasing, although in the case of the Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalyst after catalysis (see Fig 3b) it decreased a little but just to form a valley after a peak and then it continued to increase as in the other cases never coming back to zero. It follows that, in the middle region temperature, the H<sub>2</sub> uptake did not stop but it was still in progress, meaning that any reduction, of a single or multiple species, continued to occur and, as a whole, proceeded slowly as a continuum. It can be suggested, in agreement with literature [34,35], that the reduction of supported PtO<sub>x</sub> and Rh<sub>x</sub>O<sub>y</sub> species can mainly occur along this range of temperatures, as the Pd oxide-like species are prevalently reduced in the lower temperature range.

In the higher temperature region (from 265°C up to 500°C), a large and clearly defined peak at ca. 370°C was present in the TPR profiles of both catalysts either as fresh material or after catalysis (see Fig. 3). According to literature [35], such a large peak at ca. 375°C can be mainly due to Rh<sub>x</sub>O<sub>y</sub> species which are more strongly interacting with the supports. However, it cannot be excluded that also some residual PtO<sub>x</sub> or even PdO<sub>x</sub> species more strongly interacting with the support can be reduced at higher temperature, thus contributing to the peak at ca. 375°C. In spite of the drift of the baseline, which seems to be a characteristic of the TPR profiles of supported noble metals systems [32, 36], an estimate of the total H<sub>2</sub> consumption was made and it was in good agreement with the theoretical H<sub>2</sub> consumption under the hypothesis that PdO, PtO and Rh<sub>2</sub>O<sub>3</sub> were the oxide-like species formed after calcination at 500°C (see Table 1). On the basis of the total H<sub>2</sub> consumption and in agreement with the results reported in literature, it can be reasonably suggested that, in both Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts, the noble metals were fully reduced to the metal state at the end of the TPR runs, at least under our experimental conditions.



**Fig. 2.** FESEM images of Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts as prepared (section a, In-Lens detector), after the catalytic tests (section b, In-Lens detector) and after catalysis in the presence of H<sub>2</sub>O (section c, Back Scattering detector). The EDX elemental maps (coloured images) are reported in section a (referring to the dotted marked area) for Zr, Ti, Ce, Pt, Pd and Rh, in section b for Pt, Pd and Rh, and in section c for Pd.

However, besides the common features described above, the TPR profiles of both catalysts after the catalytic runs evidenced also some differences (see Fig. 3). In particular, a shift from ca. 370°C to ca. 400°C of the largest peak present in the higher temperature side was evident, very likely related to a strengthening of the Rh<sub>x</sub>O<sub>y</sub>-support interaction. This effect suggested that structural changes of the Rh species occurred

in consequence of the redox cycles along the SCR<sub>sim</sub> reaction. Indeed, such a dynamic redox behavior of Rh species has been recently reported for a Rh/Al<sub>2</sub>O<sub>3</sub> catalyst in a very elegant paper showing that structural changes of Rh species due to complex reduction/oxidation processes of oxide-like and metal-like Rh particles can occur under a reactant stream simulating a Three-Way Catalytic Reaction [9]. Additionally, the rising

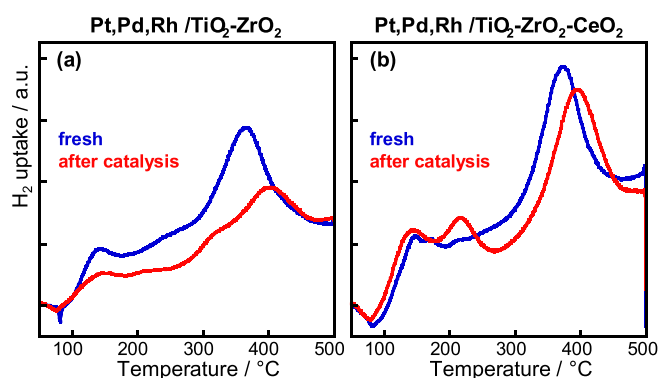


Fig. 3. TPR profiles of (section a) Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and (section b) Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts, either as fresh material or after the catalytic runs.

up of a shoulder at ca. 300°C for Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> catalyst and of a better defined peak at ca. 225°C for the Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalyst were evident. These effects can be related to some changes in size and/or morphology of the Pd and Pt oxide-like particles during the catalytic reactions and/or to a different interaction with the support. Moreover, the TPR quantitative analysis of the catalysts after catalytic runs suggests that the oxidizing pre-treatment did not convert the catalysts to their initial fully oxidized state. These findings, as a whole, suggest that, along the catalytic runs, some changes of the nature of the catalysts occurred.

### 3.3. In situ FTIR analysis of the surface species using NO or CO as probe molecules

FTIR spectra of both Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts, recorded at room temperature upon adsorption of NO at increasing pressure ( $0.5 \leq \text{NO} \leq 100$  Torr), showed a progressive increase of various peaks in the frequency range 1950–1700 cm<sup>-1</sup> (Fig. 4a). Additionally, small contributions at about 2250 cm<sup>-1</sup> and in the 1620–1550 cm<sup>-1</sup> region and a negative peak at 1356 cm<sup>-1</sup>, coupled to a positive peak at 1345 cm<sup>-1</sup>, appeared in the spectra. Peaks in the range 1950–1700 cm<sup>-1</sup> can be attributed to nitrosyls adsorbed on the various atomic species present on the catalyst surface. At low NO pressure values (<1 Torr), the peaks appearing first were those in the range 1835–1700 cm<sup>-1</sup>, which have been assigned to neutral nitrosyls formed on cationic or metal sites (like Pd<sup>n+</sup>, Rh<sup>+</sup>, Pt<sup>0</sup> and Rh<sup>0</sup>) [37–40]. The

most intense peak at about 1800 cm<sup>-1</sup> and the couple of peaks at 1830 and 1740 cm<sup>-1</sup> are usually ascribed to Rh-NO and Rh-(NO)<sub>2</sub> gem-dinitrosyls, respectively [37], thus suggesting that, among noble-metals, Rh exposed sites yielded the most stable nitrosyl complexes and has at least two coordinative unsaturations. At intermediate pressure values (<10 Torr), the peak at ca. 1940 cm<sup>-1</sup>, assigned to Pt<sup>2+</sup>-NO [37], and the peak at 1914 cm<sup>-1</sup>, attributed to positively charged Rh<sup>0</sup>-NO<sup>+</sup> [38,39], increased. At the higher pressure values ( $\leq 100$  Torr), the peak at 1901 cm<sup>-1</sup> can be assigned to a labile Ti<sup>4+</sup>-NO species which markedly increased and then disappeared after outgassing. As a whole, such a plethora of peaks are clearly indicating that many coordinatively unsaturated sites (CUS) existed on the surface of noble metal particles and that Rh yields the strongest interaction with NO.

The contributions at 2250 cm<sup>-1</sup> and in the 1620–1550 cm<sup>-1</sup> region (see Fig. 4a) were due to adsorbed N<sub>2</sub>O and adsorbed nitrite/nitrate species, respectively, originating from NO disproportionation on the oxide surface [40]. The amount of such species was rather large in the CeO<sub>2</sub>-containing Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalyst (see Fig. 4a), for which more defined bands of bidentate nitrate species (about 1570, 1330 and 1180 cm<sup>-1</sup> [40]) appeared. This result suggests that CeO<sub>2</sub> enhanced the interface reactivity, promoting the NO disproportionation on its reactive surface O sites. Finally, the coupled negative/positive peaks arose from the red-shift of an adsorption mode, probably of a surface termination, as a titanyl-like Ti=O species [41], interacting with an adjacent electron-withdrawing species, as the adsorbed nitrites/nitrates. A similar red-shift has been already reported for the stretching mode of S=O in sulphate species covalently bonded to the surface of oxides [42].

In the case of CO adsorption at RT (Fig. 4b), bands in the carbonyl region of 2220–1950 cm<sup>-1</sup> and in the carbonates region below 1650 cm<sup>-1</sup> appeared in the spectra of both Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts, the intensity of all bands increasing with increasing CO pressure. In particular, the peaks in the range 2205–2185 cm<sup>-1</sup>, assigned to labile carbonyls (bonded through  $\sigma$ -donation) on TiO<sub>2</sub> and ZrO<sub>2</sub> supports, are the most sensitive to CO pressure, markedly increasing as CO pressure increased and disappearing on evacuation (dotted lines in Fig. 4b). The adsorption on TiO<sub>2</sub> typically occurred on two types of CUS,  $\alpha$ -Ti<sup>4+</sup> and  $\beta$ -Ti<sup>4+</sup>, yielding peaks at about 2205 and 2190 cm<sup>-1</sup> [43], while the adsorption on Zr<sup>4+</sup> gave rise to a band at 2200–2190 cm<sup>-1</sup>, red-shifting as CO pressure increased [44]. The band envelope at lower wavenumbers (2190–2000 cm<sup>-1</sup> region), progressively increasing as CO pressure increased, are due to more stable carbonyls (bonded through  $\sigma$ -donation reinforced by  $\pi$ -back donation) as,

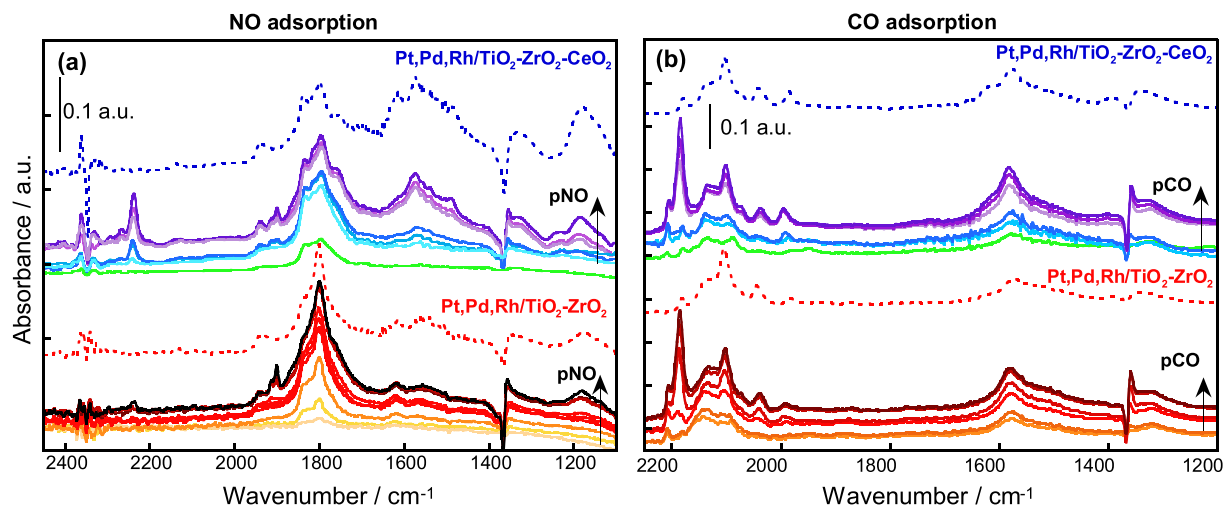


Fig. 4. FTIR spectra, gas subtracted, after (section a) NO and (section b) CO adsorption at RT on activated Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts at increasing equilibrium pressure (from 0.050 to 100 Torr) and after evacuation for 5 min (dotted lines).



differently from carbonyls on the support sites, they are nearly unaffected by evacuation. The envelope consisted of several peaks (at 2180, 2160, 2136, 2100, 2090, 2075, and 2036  $\text{cm}^{-1}$ ) assignable to different types of (i) linear carbonyls on oxidised ( $\text{Pt}^{2+}$ ,  $\text{Pd}^{n+}$  and  $\text{Rh}^+$ , peaks above 2100  $\text{cm}^{-1}$ ) and on reduced ( $\text{Pt}^0$ ,  $\text{Pd}^0$  and  $\text{Rh}^0$ , peaks below 2100  $\text{cm}^{-1}$ ) noble-metal sites and of (ii) bridged carbonyls on reduced sites (about 1998  $\text{cm}^{-1}$ ) [37,45–48]. At the higher CO pressure, the bands at 2100 and 2036  $\text{cm}^{-1}$  become predominant in the envelope and have been assigned to a gem-dicarbonyl  $\text{Rh}^+(\text{CO})_2$  complex ( $\nu_{\text{asym}}$  and  $\nu_{\text{sym}}$ ) on isolated  $\text{Rh}^+$  sites [49], confirming that the degree of coordinative unsaturation for the Rh exposed surface sites is at least two. Bands typical of carbonates (1580, 1320 and 1050  $\text{cm}^{-1}$  [50]) and the coupled negative/positive peaks (1370 and 1360  $\text{cm}^{-1}$ ) appeared in the spectral region below 1650  $\text{cm}^{-1}$  (see Fig. 4b). It should be noted that the simultaneous formation of carbonates and of carbonyls formed on (fully or partially) reduced noble-metal atoms indicated a surface reaction in which surface noble-metal ions are reduced by CO with a consequent formation of  $\text{CO}_2$  that yielded adsorbed carbonates. This process occurred promptly as CO contacted the samples even at low pressure, pointing to the presence of highly reactive surface oxygen species that are available for interface redox processes even at room temperature. The coupled negative/positive peaks, already observed after NO adsorption (vide supra), were in this case possibly due to the interaction of the previously suggested surface  $\text{Ti}=\text{O}$  species with an adjacent adsorbed electron-withdrawing carbonate.

In order to shed more light on the surface redox properties, CO was used simultaneously as a reducing agent and as a probe molecule. To this purpose, the catalysts were first heated at different temperatures (from

100 to 300°C) in CO at a fixed pressure (ca. 100 Torr). After treatment at each temperature, the spectrum was recorded at RT after cooling in CO.

In the case of the Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> catalyst (Fig. 5a), upon heating in CO some remarkable changes in the spectra occurred in the noble-metal carbonyl region (2180–1990  $\text{cm}^{-1}$ ), while bands from carbonyls on the support sites remained practically the same. In particular, heating in CO up to 150°C, the intensity of weak bands from oxidized noble-metal carbonyls (2180–2100  $\text{cm}^{-1}$ ) decreased, whereas the bands of reduced noble-metal carbonyls (2100–1990  $\text{cm}^{-1}$ ) and those of  $\text{Rh}^+(\text{CO})_2$  dicarbonyls (2100 and 2036  $\text{cm}^{-1}$  [49]) increased. It should be noted that  $\text{Rh}^+(\text{CO})_2$  dicarbonyls reached their maximum intensity at 150°C. This trend, together with the increase of carbonate bands intensity (around 1600  $\text{cm}^{-1}$  [50]), proves that an additional fraction of the surface noble-metal ions was progressively reduced as the temperature increased. This is also supported by the formation of bridged carbonyl species (broad band at about 1880  $\text{cm}^{-1}$ ), which typically formed on metal species. On increasing the temperature up to 250°C, the  $\text{Rh}^+(\text{CO})_2$  dicarbonyl bands progressively decreased while a band at about 2050  $\text{cm}^{-1}$ , likely ascribed to  $\text{Rh}^0\text{-CO}$  species [51], increased. At 300°C carbonyls on noble metal species almost disappeared, suggesting that dissociative chemisorption of CO occurred poisoning the adsorbing sites.

For the sample Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub>, although a similar trend upon CO thermal treatment occurred, some important differences can be noticed with respect to the Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> (Fig. 5b): (i) the  $\text{Rh}^+(\text{CO})_2$  dicarbonyl bands reached the maximum intensity at higher temperature (200°C vs. 150°C), (ii)  $\text{Rh}^0\text{-CO}$  formation was evidenced at higher temperature (250°C vs. 200°C), and (iii) bridged carbonyls on metal species (1880  $\text{cm}^{-1}$ ) formed in a negligible amount. All these findings suggested that the  $\text{Rh}_x\text{O}_y$  species were less reducible in the presence of CeO<sub>2</sub>.

As a whole, from these findings it can be suggested that the surface species exposed on the surface of the noble metal oxide-like particles are characterized by a different reducibility. Among the exposed surface species, the  $\text{Rh}_x\text{O}_y$  are likely the least reducible ones, being stabilised as  $\text{Rh}^+$ . These conclusions are in agreement with the analysis of the TPR results showing that the  $\text{Rh}_x\text{O}_y$  species reduced at higher temperature while the  $\text{PdO}_x$  and  $\text{PtO}_x$  oxide-like species reduced at lower temperatures (see Fig. 3), the reduction of  $\text{PdO}_x$  occurring first (vide supra). Also the FTIR evidenced that  $\text{Rh}_x\text{O}_y$  species are less reducible in the presence of CeO<sub>2</sub>, in very good agreement with the TPR results.

#### 3.4. Catalytic activity

##### 3.4.1. Simultaneous abatement of NO and N<sub>2</sub>O with CH<sub>4</sub> in presence (SCR<sub>sim</sub>) or absence (CR<sub>sim</sub>) of O<sub>2</sub>

The O<sub>2</sub> content in the NO+N<sub>2</sub>O+CH<sub>4</sub>+O<sub>2</sub> mixture (SCR<sub>sim</sub>) markedly affected the activity and selectivity of the Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts for the simultaneous abatement of NO and N<sub>2</sub>O with CH<sub>4</sub>. When the O<sub>2</sub> content was 2500 ppm, a good activity and a good CO<sub>2</sub> selectivity (>90% over the entire temperature range) for the SCR<sub>sim</sub> were found on both catalysts (Fig. 6). Indeed, in such conditions they were effective for the conversion of NO and N<sub>2</sub>O to N<sub>2</sub> that sharply increased as the temperature increased and reached their maximum value (about 90% and about 100%, respectively) at 425°C on Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> catalyst and at 400°C on Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalyst (see Fig. 6). Such a small difference of temperature may be ascribed to the presence of ceria that, due to its well-known ability to give rise to oxygen vacancies and reactive oxygen species [30], can improve the redox properties of the Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalyst, and consequently, the catalytic activity. In the case of NO, above ca. 400°C the conversion decreased to some extent forming a depressed curve with a minimum, which was more evident for Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> (70%, see Fig. 6), suggesting the formation of by-products. Since the C-balance remained at 100%, the eventually formed species are only N-containing by-products (like NH<sub>3</sub>).

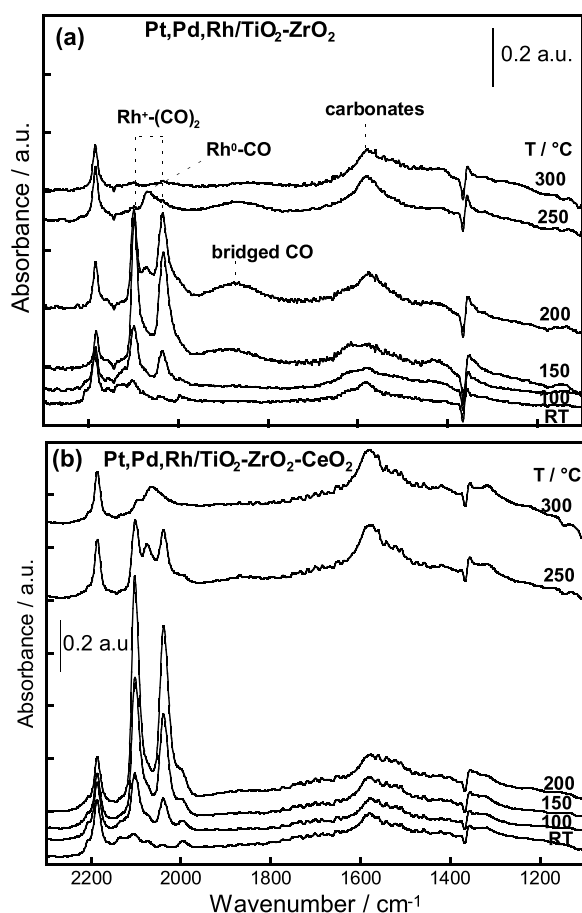
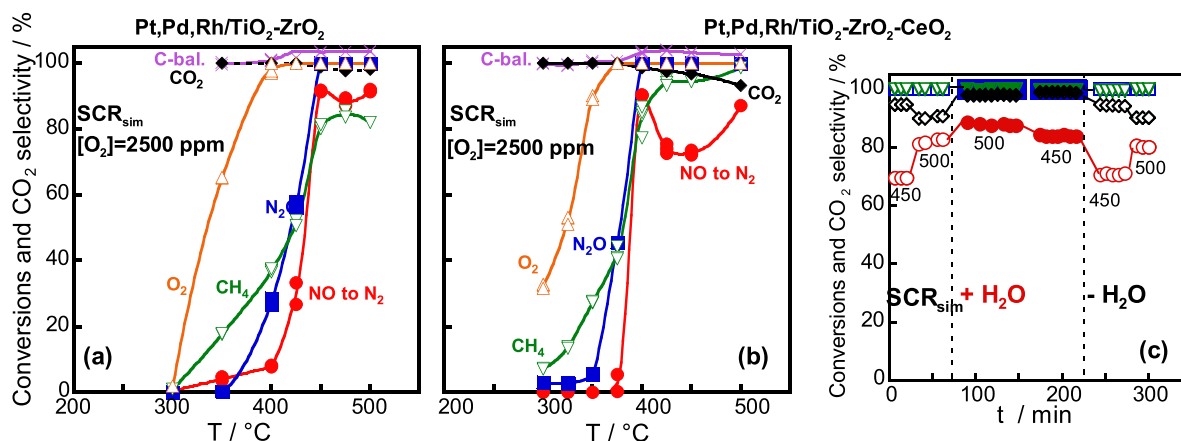


Fig. 5. *In situ* FTIR spectra after CO adsorption at room temperature (RT) and subsequent heating in CO at increasing temperature up to 300°C (stepwise of 50°C) on activated (section a) Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and (section b) Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts.



**Fig. 6.** The activity for simultaneous abatement of NO and N<sub>2</sub>O with CH<sub>4</sub> in the presence of O<sub>2</sub> as a function of temperature on (section a) Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and (section b) Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> under dry feed. For the last sample, the activity under dry (open symbols) or wet feed (containing 2.5 % v/v of water vapour, solid symbols) was reported as a function of exposure time to the feed (section c). NO to N<sub>2</sub> (●), N<sub>2</sub>O (■), CH<sub>4</sub> (▽) and O<sub>2</sub> (△) conversions, CO<sub>2</sub> selectivity (◆), C-balance (×) as a function of temperature or time. Reactants concentration: [N<sub>2</sub>O]=[NO]=[CH<sub>4</sub>]=4000 ppm, [O<sub>2</sub>]=2500 ppm, [H<sub>2</sub>O]=25000 ppm (if present); total flow rate=100 cm<sup>3</sup> STP/min, He as balance.

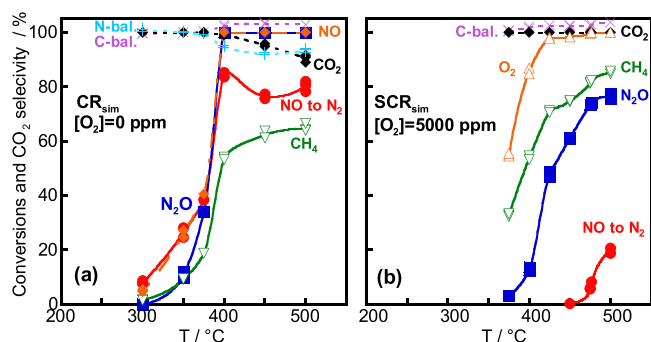
When water (2.5% v/v) was added to the NO+N<sub>2</sub>O+CH<sub>4</sub>+O<sub>2</sub> mixture to simulate nearly real conditions, the catalytic behaviour for the ceria-containing catalyst was not negatively but positively affected (Fig. 6c). In particular, at 500°C and 450°C the N<sub>2</sub>O and CH<sub>4</sub> conversions remained at 100% while the NO conversion and the CO<sub>2</sub> selectivity were even better in the presence of water. Moreover, when water was removed from the stream, the Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalyst went back to the original catalytic activity (see Fig. 6c), suggesting that in the presence of water the active sites were preserved sustaining a catalytic behaviour at least as good as shown before water was added. This is somewhat expected being an usual behaviour of the TWC's reported in literature as outlined in a study of the three-way behaviour of platinum-alumina-ceria catalysts [52]. In this paper the increase of NO abatement activity when water was added to an exhaust-simulating feed stream has been justified by two factors: (i) the occurrence of the water-gas shift reaction, enhanced by cerium oxide, making weaker the CO adsorption on metal platinum active sites and, as a consequence, decreasing its self-poisoning effect; (ii) NO can react also with the products of the water-gas shift reaction.

When O<sub>2</sub> was absent from the mixture (i.e. NO+N<sub>2</sub>O+CH<sub>4</sub>, CR<sub>sim</sub>), both catalysts showed almost the same catalytic behaviour. In Fig. 7a the results for the Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> catalyst are presented as a representative sample. If compared to the SCR<sub>sim</sub> reaction with 2500 ppm of

O<sub>2</sub>, the CR<sub>sim</sub> was slightly less effective due to selectivity issues. Indeed, the N<sub>2</sub>O and the total NO conversions, starting at about 300°C together with the CH<sub>4</sub> conversion, were about 100% above 400°C, but the NO conversion to N<sub>2</sub> was lower, being about 80% in the same temperature range (Fig. 7a). Moreover, the CO<sub>2</sub> selectivity decreased at 85% as the temperature increased to 500°C due to CO formation. It should be noted that, above ca. 375°C, while the C-balance was always 100%, the N-balance was nearly 90%, confirming that, as for the SCR<sub>sim</sub> (vide supra), a small amount of only N-containing by-products (like NH<sub>3</sub>) was formed.

By contrast, when O<sub>2</sub> in the mixture was 5000 (or 10000 ppm), the SCR<sub>sim</sub> was not effective over the entire range of temperature explored (250-500°C). In particular, at 5000 ppm of O<sub>2</sub>, the N<sub>2</sub>O conversion reached ca. 80% only at 500°C and the NO conversion to N<sub>2</sub> was at most 20% at the same temperature (see Fig. 7b). On increasing the amount of O<sub>2</sub> to 10000 ppm, the situation became worse because, while the N<sub>2</sub>O conversion remained similar, the NO conversion became negligible. Literature data supported our results on the effect of the O<sub>2</sub> content in the reactant mixture. Indeed a similar trend was observed for the NO conversion on Rh/ZrO<sub>2</sub> [53] as well as on Ce-Zr promoted Pd-Rh/Al<sub>2</sub>O<sub>3</sub> catalysts [28], showing that the NO conversion decreased monotonically on increasing air to fuel (A/F) ratio.

It is relevant to note that the CH<sub>4</sub> conversion in SCR<sub>sim</sub>, either at O<sub>2</sub> content of 2500 or 5000 ppm, started on both catalysts at ca. 250°C together with the conversion of O<sub>2</sub>, well before the temperature range at which the N<sub>2</sub>O and NO started to be converted (about 350-375°C, see Figs. 6 and 7b). This finding suggests that from 250°C up to 350-375°C only the competitive CH<sub>4</sub> combustion occurred. It should be pointed out that, even at the lowest O<sub>2</sub> amount (2500 ppm) at which the best activity and selectivity were found, N<sub>2</sub>O and NO started to be converted only when O<sub>2</sub> was almost completely consumed by CH<sub>4</sub>. After this point, the remaining CH<sub>4</sub> continued to react with NO and N<sub>2</sub>O until they were almost completely converted above 400°C (see Fig. 6). The presence of O<sub>2</sub> in the feed is important in order to guarantee the CO<sub>2</sub> selectivity at a value of 100% on Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and at values higher than 90% on Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> over the entire temperature range (see Fig. 6).



**Fig. 7.** Simultaneous abatement of NO and N<sub>2</sub>O with CH<sub>4</sub> in the absence (CR<sub>sim</sub>, section a) and in the presence of O<sub>2</sub> (SCR<sub>sim</sub>, section b) on Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>. NO to N<sub>2</sub> (●), N<sub>2</sub>O (■), CH<sub>4</sub> (▽), O<sub>2</sub> (△) conversions, CO<sub>2</sub> selectivity (◆), C-balance (×) and N-balance (+) as a function of temperature. Reactants concentration: [N<sub>2</sub>O]=[NO]=[CH<sub>4</sub>]=4000 ppm, [O<sub>2</sub>]=0 or 5000 ppm (total flow rate=100 cm<sup>3</sup> STP/min, He as balance).

### 3.4.2. SCR<sub>N2O</sub>, SCR<sub>NO</sub>, CR<sub>N2O</sub>, CR<sub>NO</sub> and related reactions

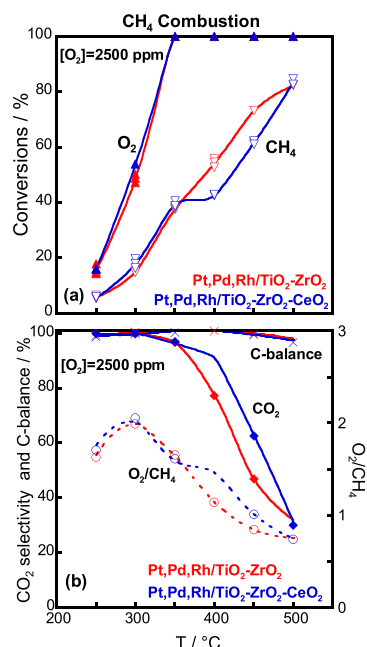
In order to have more insight into the catalytic behaviour of both Pt, Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts for the SCR<sub>sim</sub> reaction, the activity for the main competitive side-reaction, i.e. CH<sub>4</sub> combustion (CH<sub>4</sub>+O<sub>2</sub>), was investigated. Moreover, for the same purpose, the separate abatement reactions of NO or N<sub>2</sub>O, either in the absence (CR<sub>NO</sub>, CR<sub>N2O</sub>) or in the presence of different amount of O<sub>2</sub>



(SCR<sub>NO</sub>, SCR<sub>N<sub>2</sub>O</sub>), as well as the N<sub>2</sub>O decomposition, by itself or in the presence of O<sub>2</sub> or NO, were also investigated.

**CH<sub>4</sub> combustion.** Both catalysts were very active for the CH<sub>4</sub> combustion at the O<sub>2</sub> content of 2500 ppm, the value at which the best performance for SCR<sub>sim</sub> was observed. The light-off temperature of the CH<sub>4</sub> combustion was at ca. 200°C. On increasing temperature, O<sub>2</sub> conversion became 100% already at 325°C while the CH<sub>4</sub> conversion was still increasing (Fig. 8a). Moreover, above 350°C on both catalysts the CO<sub>2</sub> selectivity markedly decreased, with only CO and CO<sub>2</sub> observed as reaction products (Fig. 8b). It should be noted that, at this low amount of O<sub>2</sub> in the mixture (much less than the stoichiometric value for total combustion), the decrease of the CO<sub>2</sub> selectivity, the simultaneous decrease of the O<sub>2</sub>/CH<sub>4</sub> values and the full C-balance (Fig. 8b) occurred all together. How can this combination of factors be explained? A reasonable explanation, supported by literature, can be that some syngas (CO+H<sub>2</sub>) was formed through CH<sub>4</sub> partial oxidation, in agreement with the well-recognised activity of noble metals for this reaction [51]. The evidence found that the CH<sub>4</sub> combustion light-off occurred at 200°C, a temperature at which in the SCR<sub>sim</sub> with O<sub>2</sub> at 2500 ppm N<sub>2</sub>O and NO were both not yet converted while the CH<sub>4</sub> and O<sub>2</sub> conversions already occurred (see Fig. 6), is confirming that in the lower temperature range of the SCR<sub>sim</sub> the competitive CH<sub>4</sub> combustion took place.

As anticipated in our previous work [27], Pd and Pt are very likely the main species responsible for total oxidation of methane, acting possibly in a synergism [8]. In particular, Pd, or the Pd-PdO<sub>x</sub> interface, is considered to be one of the most active materials for this reaction in lean combustion conditions [54,55], also in the presence of NO [56]. The combustion activity has been directly related to the PdO reducibility strongly affected by the support that influenced the Pd-O bond strength [55]. Moreover, it has been reported that the Pd activity increases with the increase of the oxygen vacancies on the PdO surface [57]. Since, as evidenced by the TPR results, the Pd species are the most easily reducible metal ion species in the catalysts, it is reasonable that Pd metal, likely together with Pt, is formed by reduction with CH<sub>4</sub> not only during combustion but also along the SCR<sub>sim</sub>, as confirmed by the XRD analysis (vide supra).

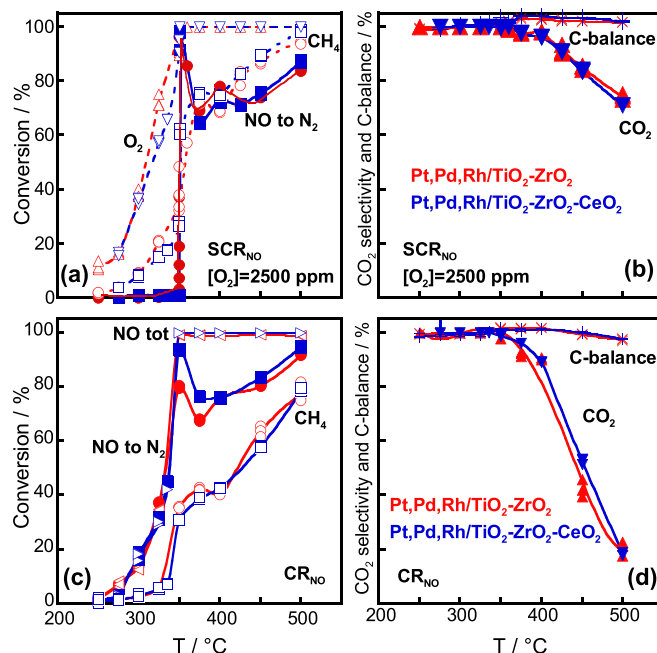


**Fig. 8.** CH<sub>4</sub> combustion on Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub>. CH<sub>4</sub> (▽) and O<sub>2</sub> (▲) conversions (section a), CO<sub>2</sub> selectivity (◆), C-balance (×) and O<sub>2</sub>/CH<sub>4</sub> ratio (○) as a function of temperature (section b). Reactants concentration: [CH<sub>4</sub>]=4000 ppm, [O<sub>2</sub>]= 2500 ppm (total flow rate=100 cm<sup>3</sup> STP/min, He as balance).

**SCR<sub>NO</sub> and CR<sub>NO</sub> reactions.** On both Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts, the separate NO abatement in the presence of O<sub>2</sub> (SCR<sub>NO</sub>) at 2500 ppm, at which the best performance for SCR<sub>sim</sub> was observed, showed a behaviour similar to that found in absence of O<sub>2</sub> (CR<sub>NO</sub>). However, some differences can be noticed. Although both catalysts were active for NO reduction by CH<sub>4</sub>, with a similar activity either for the SCR<sub>NO</sub> (Fig. 9a and b) or CR<sub>NO</sub> (Fig. 9c and d), a remarkable difference was observed for the light-off temperature. It was 350°C for SCR<sub>NO</sub>, with a very steep increase of the NO conversion to N<sub>2</sub> from 0 to 100% in a very short range of temperature (see Fig. 9a) occurring when O<sub>2</sub> was completely consumed by CH<sub>4</sub>. On the other hand, the light-off temperature for the CR<sub>NO</sub> occurred at much lower temperature (250°C) with a gradual increase of the NO conversion to N<sub>2</sub> which became 100% at the same temperature observed for SCR<sub>NO</sub> (350°C, Fig. 9c). The difference in the light-off temperature in the separate NO abatement reactions is confirming the inhibiting effect of O<sub>2</sub> on the NO conversion already observed in the SCR<sub>sim</sub>.

However, above 350°C the NO conversion to N<sub>2</sub> decreased going through a minimum in both SCR<sub>NO</sub> and CR<sub>NO</sub> reactions, thus indicating the formation of some N-containing by-products. Since the C-balance was nearly 100% in the whole temperature range explored, the N-containing by-products are not containing C species (likely NH<sub>3</sub>, since N<sub>2</sub>O was never detected). On the other hand, CH<sub>4</sub> conversion, starting at 250°C for both reactions, increased with increasing temperature all along the temperature range (Fig. 9a and c). Above 350°C, side-reactions consuming CH<sub>4</sub> but yielding CO occurred as proved by the trend of the CO<sub>2</sub> selectivity. In particular, CO<sub>2</sub> selectivity decreased from 100% to 70% at 500°C in the case of SCR<sub>NO</sub>, while it markedly decreased from 100% to 20% for CR<sub>NO</sub> (Fig. 9d). It can be noticed that the presence of O<sub>2</sub>, although having a negative effect due to the inhibition of the NO conversion light-off, plays a positive role improving the CO<sub>2</sub> selectivity.

Both these effects were still observed to a higher extent in the SCR<sub>NO</sub>



**Fig. 9.** SCR<sub>NO</sub> (sections a and b) and CR<sub>NO</sub> (sections c and d) reactions on Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> (red symbols) and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> (blue symbols) catalysts. NO to N<sub>2</sub> (●, ◐), total NO (<math>\triangleleft, \triangleright</math>), CH<sub>4</sub> (◻, ◊) and O<sub>2</sub> (▲, ▽) conversions as a function of temperature (sections a and c); CO<sub>2</sub> selectivity (▲, ▼), and C-balance (×, +) as a function of temperature (sections b and d). The first symbols in parentheses refer to Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>, the second ones to Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub>. Reactants concentration: [NO]=[CH<sub>4</sub>]=4000 ppm, [O<sub>2</sub>]= 0 or 2500 ppm (total flow rate=100 cm<sup>3</sup> STP/min, He as balance).

on increasing the O<sub>2</sub> amount from 2500 to 5000 and 10000 ppm. If compared to the SCR<sub>NO</sub> at 2500 ppm of O<sub>2</sub>, the light-off temperature shifted to higher values for O<sub>2</sub> at 5000 ppm (about 375°C) and even NO conversion never occurred at 10000 ppm (Supplementary Fig. 1). On the other hand, the CO<sub>2</sub> selectivity remarkably improved, being almost 100% in the whole temperature range at both 5000 and 10000 ppm of O<sub>2</sub>, thus confirming the positive role of O<sub>2</sub> on this factor. By contrast, the CH<sub>4</sub> conversion was almost negligibly affected by the change of the O<sub>2</sub> content, either in the lower temperature region, where only the CH<sub>4</sub> combustion occurred as confirmed by the simultaneous starting of CH<sub>4</sub> and O<sub>2</sub> consumption, or at higher temperature, where the NO reduction also occurred (see Supplementary Fig.1b).

The inhibiting effect of O<sub>2</sub> on the NO conversion in the SCR<sub>NO</sub> can be explained by taking into account two different activation processes for CH<sub>4</sub> and NO on the catalyst surface. If, on the one hand, the CH<sub>4</sub> activation is occurring on the surface of noble metal oxide-like particles [54–56], on the other hand, the NO activation occurred on a CH<sub>4</sub>-reduced noble metal surface, this being supported by the fact that the NO reduction is starting only when O<sub>2</sub> was totally consumed and the surface was thus reduced by CH<sub>4</sub> (see Supplementary Fig. 1). This is in agreement with literature showing that the dissociation of NO to N<sub>(ads)</sub> and O<sub>(ads)</sub> takes place on a reduced noble metal surface with subsequent desorption of N<sub>2</sub> and removal of O<sub>(ads)</sub> by the reductant (CH<sub>4</sub> in our case) [4]. This explains why in our case on increasing the O<sub>2</sub> amount, which preserves the surface in the oxidised state despite the presence of a reductant (CH<sub>4</sub>), the NO is not any longer activated and therefore converted. In particular, Rh metal in the three-way Rh-Pd-Pt-containing catalysts was found to be effective for the NO reduction under streams simulating Three-Way Catalytic Reaction, playing a relevant role in the NO dissociation [9,58]. Then, it can be suggested that Pd and Pt, which are considered to promote the CH<sub>4</sub> oxidation reaction [57,58] are mainly responsible for the activation of CH<sub>4</sub>, while Rh could be

responsible for NO activation.

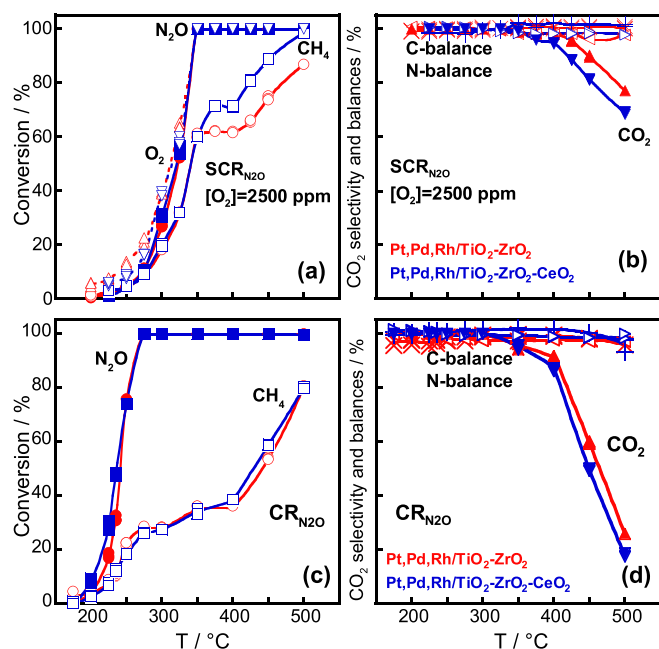
**SCR<sub>N2O</sub> and CR<sub>N2O</sub> reactions.** The study of the N<sub>2</sub>O abatement by CH<sub>4</sub> in the absence of NO and at the O<sub>2</sub> content of 2500 ppm, at which the best performance for SCR<sub>sim</sub> was observed (SCR<sub>N2O</sub>), showed that Pt, Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts were both active and selective for N<sub>2</sub>O reduction (Fig. 10a and b). In particular, all the reactants (i.e. N<sub>2</sub>O, CH<sub>4</sub> and O<sub>2</sub>) started to be converted at approximately the same temperature (ca. 225°C). At 350°C, the conversions of N<sub>2</sub>O and O<sub>2</sub> were complete while, at the same temperature, the CH<sub>4</sub> conversion reached ca. 60% with 100% CO<sub>2</sub> selectivity. It can be noticed that, if compared with the homologous SCR<sub>NO</sub> reaction starting only when O<sub>2</sub> was completely consumed by CH<sub>4</sub>, in the SCR<sub>N2O</sub> the catalyst was selective for N<sub>2</sub>O conversion with respect to combustion above 325°C up to 400°C (matching the 2N<sub>2</sub>O + CH<sub>4</sub> + O<sub>2</sub> → 2N<sub>2</sub> + CO<sub>2</sub> + 2H<sub>2</sub>O stoichiometry), whereas below 325°C the competitive CH<sub>4</sub> combustion occurred to a small extent (as suggested by the stoichiometric ratios in Supplementary Fig. 2a). At higher temperature O<sub>2</sub> was also formed, leading to a decrease of CO<sub>2</sub> selectivity, and the CH<sub>4</sub> conversion increased further (up to 80 and 100% for the Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt, Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts, respectively, Fig. 10a and b), thus suggesting that side-reactions occurred.

Some further new insight was provided by the comparison of the abatement of N<sub>2</sub>O by CH<sub>4</sub> with or without O<sub>2</sub> (SCR<sub>N2O</sub> vs CR<sub>N2O</sub>, Fig. 10). The N<sub>2</sub>O conversion in CR<sub>N2O</sub>, if compared to that found in the SCR<sub>N2O</sub> reaction at 2500 ppm of O<sub>2</sub>, started on both catalysts at lower temperature (about 175°C vs 225°C) and became complete also at lower temperature (275°C vs 350°C), showing that O<sub>2</sub> has an inhibiting effect on N<sub>2</sub>O reduction by CH<sub>4</sub>, as already found for NO. The CH<sub>4</sub> conversion in CR<sub>N2O</sub> reached ca. 25% at 275°C with a CO<sub>2</sub> selectivity equal to 100%. At temperatures higher than 400°C, a remarkable increase of CH<sub>4</sub> conversion (reaching about 80% at 500°C) and a strong decrease of CO<sub>2</sub> selectivity can be noticed, while the C- and N-balances remained equal to 100%. These results, as a whole, indicated that in the case of the CR<sub>N2O</sub> reaction the only side-reactions occurring at high temperatures (above ca. 400°C) were those consuming CH<sub>4</sub> and yielding undesired CO as a product of its partial oxidation.

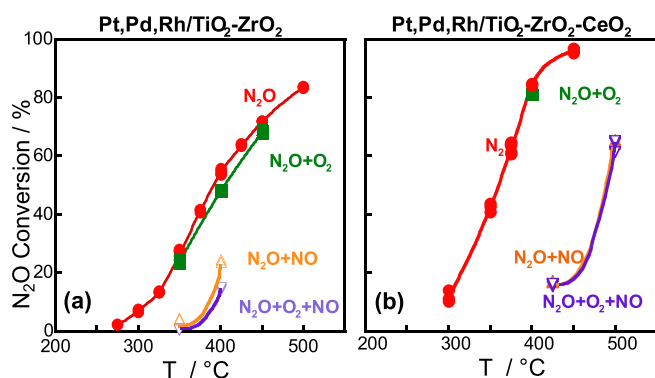
The further increase of O<sub>2</sub> content in the SCR<sub>N2O</sub> feed from 2500 to 5000 or 10000 ppm (Supplementary Fig. 3) somewhat decreased the N<sub>2</sub>O conversion that, at 10000 ppm, never reached completeness even at 500°C. On the other hand, O<sub>2</sub> in excess remarkably improved the CO<sub>2</sub> selectivity, which was equal to 100% in the whole temperature range explored. It is interesting to note that, at O<sub>2</sub> contents of 5000 and 10000 ppm, the catalyst remained very selective for N<sub>2</sub>O reduction and the CH<sub>4</sub> combustion, as a side-reaction, never occurred even when O<sub>2</sub> was in large excess (10000 ppm), this being supported by the fact that the ratio O<sub>2</sub>/CH<sub>4</sub> remained constant over the whole temperature range (Supplementary Fig. 2b and c). In particular, at 10000 ppm of O<sub>2</sub>, O<sub>2</sub> is involved only in the SCR<sub>N2O</sub> reaction, although with a different stoichiometry (N<sub>2</sub>O + CH<sub>4</sub> + 3/2 O<sub>2</sub> → N<sub>2</sub> + CO<sub>2</sub> + 2 H<sub>2</sub>O). These results, as a whole, suggest that the N<sub>2</sub>O always prevails on O<sub>2</sub> for the oxidation of active sites reduced by CH<sub>4</sub>, i.e. O<sub>2</sub> does not compete with the N<sub>2</sub>O adsorption sites.

**N<sub>2</sub>O decomposition.** In order to shed more light on the N<sub>2</sub>O-involving reactions and to get more information on the N<sub>2</sub>O molecule activation, the N<sub>2</sub>O decomposition was studied on both catalysts as a probe reaction. Moreover, the effect of the addition of other molecules (NO, O<sub>2</sub>, NO + O<sub>2</sub>) to the N<sub>2</sub>O feed was investigated. It is well known that gaseous N<sub>2</sub>O is dissociatively adsorbed on noble metal cationic sites having redox-properties, thus yielding N<sub>2</sub> and reactive surface O<sub>ads</sub> species [59]. The pairing of O<sub>ads</sub> species to form gaseous O<sub>2</sub> is generally considered as the rate-limiting step and it is strongly dependent on the O<sub>ads</sub> mobility on the surface and on the strength of the O<sub>ads</sub>-site bonding [59].

Both Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts were active for the N<sub>2</sub>O decomposition confirming that noble-metals cationic sites characterised by a redox behaviour were present on the



**Fig. 10.** SCR<sub>N2O</sub> (sections a and b) and CR<sub>N2O</sub> (sections c and d) reactions on Pt, Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> (red symbols) and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> (blue symbols) catalysts. N<sub>2</sub>O (●,■), CH<sub>4</sub> (○,□), and O<sub>2</sub> (△,▽) conversions as a function of temperature (Section a and c); CO<sub>2</sub> selectivity (▲,▼), C-balance (×,+) and N-balance (◁,▷) as a function of temperature (sections b and d). The first symbols in parentheses refer to Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>, the second ones to Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub>. Reactants concentration: [N<sub>2</sub>O]=[CH<sub>4</sub>]=4000 ppm, [O<sub>2</sub>]=0 or 2500 ppm (total flow rate=100 cm<sup>3</sup> STP/min, He as balance).



**Fig. 11.**  $N_2O$  abatement on Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> (section a) and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> (section b).  $N_2O$  conversion vs temperature in  $N_2O$  decomposition or after addition to the  $N_2O$  feed of O<sub>2</sub> and NO, separately or together (as specified). Reactants concentration: [N<sub>2</sub>O]=4000 ppm, [NO]=0 or 4000 ppm, [O<sub>2</sub>]=0 or 2500 ppm (total flow rate=100 cm<sup>3</sup> STP/min, He as balance).

surface. However, a different activity can be noted as the total conversion was reached at 450 °C on Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalyst, while in the case of Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> catalyst only 80% of  $N_2O$  was converted at 500 °C (Fig. 11). Such a difference could be explained by the presence of CeO<sub>2</sub> which very likely improved the catalyst redox properties thus favouring the removal of O-species from the adjacent noble metal sites. This is in agreement with the known property of CeO<sub>2</sub> to store and release oxygen, as also evidenced in the CeO<sub>2</sub>-ZrO<sub>2</sub> based catalysts [58]. In the case of the Pt,Pd,Rh/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and Pt,Pd,Rh/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalysts previously studied [27], a sigmoidal shape of  $N_2O$  conversion curve as a function of temperature was characterised by a very steep increase at about 300 °C which looked like a threshold temperature. This jump was associated with a remarkable increase of the surface-O mobility, which leads to a much easier O<sub>2</sub> desorption, thus making free the sites for the  $N_2O$  activation. Differently from these systems [27], in the Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts the trend of  $N_2O$  conversion is following the Arrhenius law, thus suggesting that the surface-O mobility is not critically affected by the temperature, probably due to the effect of the different supports. By contrast, the surface-O mobility is dependent on the reactant composition.

The addition of O<sub>2</sub> to the  $N_2O$  feed did not change the  $N_2O$  decomposition activity, confirming our suggestion that O<sub>2</sub> does not compete with the  $N_2O$  adsorption sites on which the dissociative activation is proceeding (Fig. 11). It follows that, in the presence of  $N_2O$ , molecular O<sub>2</sub> in the gas phase does not contribute to the reactive surface-O coverage. Therefore, the O<sub>2</sub> inhibiting effect in the  $N_2O$  abatement by CH<sub>4</sub> (SCR<sub>N2O</sub>, see Supplementary Fig. 3) is not related to competition between O<sub>2</sub> and  $N_2O$  for the same sites, but is likely due to adsorbed intermediates formed by CH<sub>4</sub> and O<sub>2</sub> (possibly carbonates) that at lower temperatures poisoned the active sites blocking surface O-species.

Differently from O<sub>2</sub>, the addition of NO to the  $N_2O$  feed depressed the  $N_2O$  conversion, whose light-off temperature remarkably shifted from 275 °C to about 350 °C (Fig. 11). The addition of O<sub>2</sub> to the  $N_2O$ +NO mixture did not affect further the  $N_2O$  conversion. These results, as a whole, suggest that the active sites for the  $N_2O$  abatement, which are not affected by O<sub>2</sub>, are poisoned by strongly adsorbed NO-derived species blocking surface-O species, as confirmed by the *operando*-FTIR results (vide infra).

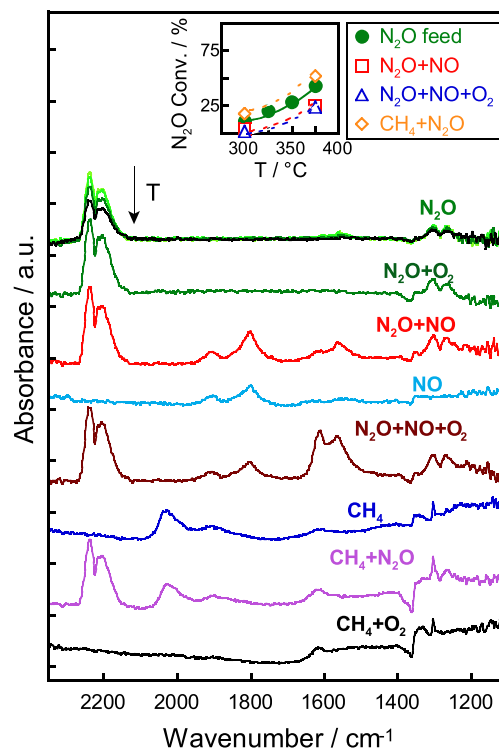
### 3.5. *Operando*-FTIR: surface species along $N_2O$ and NO abatement reactions

The evolution of the surface species formed in the presence of a flowing reactant mixture of SCR<sub>sim</sub> has been studied by means of

*operando*-FTIR experiments with the aim of identifying the intermediates responsible for the activity. To this purpose, the interaction of the single reactants (NO, N<sub>2</sub>O or CH<sub>4</sub>) and of their mixtures, with O<sub>2</sub> (2500 ppm) or in its absence, under reaction conditions has been investigated either at constant or at increasing temperature.

#### 3.5.1. NO, N<sub>2</sub>O and CH<sub>4</sub> activation

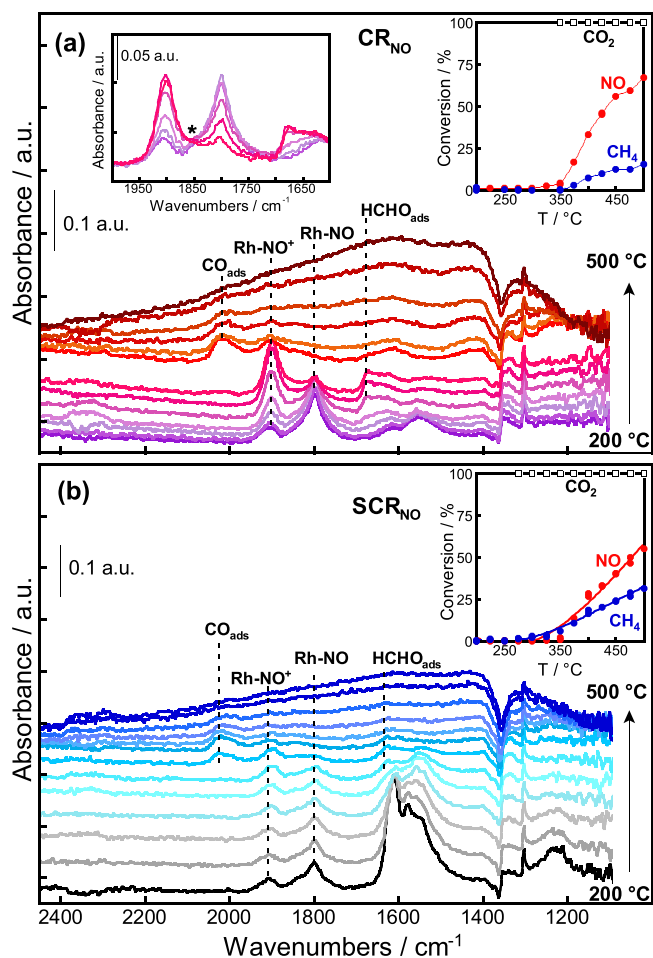
*Operando*-FTIR spectra collected on Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> as a representative sample during the  $N_2O$  decomposition at increasing temperature (Fig. 12) showed no bands of surface species besides the band of gaseous  $N_2O$  (2223 cm<sup>-1</sup>), even when O<sub>2</sub> was added to the feed. By contrast, the addition of NO to the  $N_2O$  feed at the light-off temperature of the  $N_2O$  conversion (300 °C, inset in Fig. 12) yielded either nitrosyls on noble metal sites ( $\nu_{NO}$  bands at 1906 cm<sup>-1</sup> of Rh-NO<sup>+</sup> and at 1802 cm<sup>-1</sup> of Rh-NO [38–40]) and adsorbed nitrites/nitrates (bands at 1615 and 1560 cm<sup>-1</sup>). Adsorbed nitrites/nitrates species were possibly in bridged configuration as their  $\nu_3$  mode, expected below 1200 cm<sup>-1</sup>, was not observed in the spectra [40,60]. It should be noted that in the NO feed alone only nitrosyls and a negligible amount of nitrite/nitrate species were observed (Fig. 12). Therefore, the formation of rather large amounts of adsorbed nitrites/nitrates observed in the  $N_2O$ +NO feed can be explained suggesting that the  $N_2O$  activation occurred leaving reactive adsorbed O<sub>ads</sub> species on the surface which were able to oxidize NO. These data, as a whole, can explain why the activity of the  $N_2O$  decomposition decreased when NO was added to the  $N_2O$  stream (inset in Fig. 12). Such a decrease is very likely caused by adsorbed nitrites/nitrates species which, being rather stable (bands disappeared only upon heating above 450 °C), can compete with gaseous  $N_2O$  therefore blocking its adsorption/activation on some noble metal sites. The further addition of O<sub>2</sub> to the  $N_2O$ +NO mixture, favouring the NO oxidation to NO<sub>2</sub>, caused the increase of amount of adsorbed



**Fig. 12.** *Operando*-FTIR spectra of surface species formed on activated Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> catalyst after saturation at 300 °C under different gas mixtures (as indicated). Reactants concentration: [N<sub>2</sub>O]=[CH<sub>4</sub>]=[NO]=4000 ppm, [O<sub>2</sub>]=2500 ppm (total flow=100 cm<sup>3</sup> STP/min, balance He). In the inset, the  $N_2O$  conversion at increasing temperature for different  $N_2O$ -containing feeds (N<sub>2</sub>O, N<sub>2</sub>O+NO, N<sub>2</sub>O+NO+O<sub>2</sub> and CH<sub>4</sub>+N<sub>2</sub>O) is reported.







**Fig. 14.** Operando-FTIR spectra of surface species and (insets) the corresponding catalytic results (NO and  $CH_4$  conversion and  $CO_2$  selectivity vs T) during  $CR_{NO}$  (section a) or  $SCR_{NO}$  (section b) reactions at increasing temperature, from 200 to 500 °C (stepwise 25 °C) on activated Pt,Pd,Rh/ $TiO_2$ -Zr $O_2$  catalyst. Reactants concentration:  $[NO]=[CH_4]=4000$  ppm,  $[O_2]=0$  or 2500 ppm (total flow rate=100  $cm^3$  STP/min, He as balance). In section a, the magnification of the nitrosyl region showing the isosbestic point at 1850  $cm^{-1}$  (marked with \*) is reported.

suggests that the surface of the noble metal particles still preserved a reduced state in spite of the oxidizing condition of  $SCR_{N_2O}$ .

### 3.5.3. Surface species during NO reduction with $CH_4$ as a function of temperature

In the  $NO+CH_4$  feed (Fig. 14a), in the temperature range 200–275 °C, well below the reaction light-off temperature of 350 °C, nitrosyls bands of  $Rh-NO^+$  and  $Rh-NO$  (1900  $cm^{-1}$  and 1800  $cm^{-1}$ , respectively) appeared in the spectra together with absorptions in the region 1615–1560  $cm^{-1}$ , assignable to nitrite/nitrate and/or formates. On increasing temperature, but still below the light-off value, the intensity of the  $Rh-NO$  band at ca. 1800  $cm^{-1}$  decreased while the intensity of the  $Rh-NO^+$  band at ca. 1900  $cm^{-1}$  increased. A closer analysis of the intensity of  $Rh$ -nitrosyl bands evidenced the presence of an isosbestic point at about 1850  $cm^{-1}$  (inset in Fig. 14a), indicating that the interconversion of  $Rh-NO$  into  $Rh-NO^+$  species occurred as temperature increased. This interconversion may be explained through the oxidation of  $Rh$  metal sites by the dissociative  $NO$  chemisorption, as suggested for  $Rh/SiO_2$  and  $Rh/Al_2O_3$  systems [38]. On increasing temperature, the intensity of the band in the region 1615–1560  $cm^{-1}$  slightly decreased and a new band assigned to a formaldehyde-like species appeared at 1680  $cm^{-1}$  [61], indicating that  $CH_4$  activation is occurring thus leading

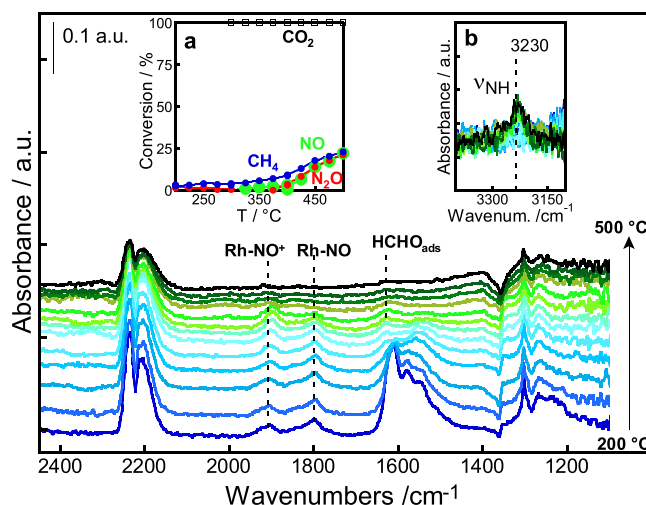
to a partially oxidized surface intermediate.

Between 350 °C and 375 °C, surface species markedly changed due to the light-off of the  $CR_{NO}$  reaction. In particular,  $Rh$ -nitrosyls and formaldehyde (or incipient  $H_2O$ ) disappeared while noble-metal linear and bridged carbonyls (bands at about 2020 and 1910  $cm^{-1}$ ) as well as a small amount of adsorbed carbonates (weak bands at about 1600 and 1400  $cm^{-1}$ ) were formed, indicating that  $CH_4$  oxidative dehydrogenation went to completion. These findings suggest that (i) below the light-off temperature, the partial  $CH_4$  dehydrogenation occurred together with the dissociative  $NO$  chemisorption that yielded reactive surface-O species, and (ii) at the light-off temperature, such reactive surface-O species were able to oxidize the formaldehyde-like species to carbonyls and  $CO_2$ .

In the  $CH_4+NO+O_2$  feed at increasing temperature ( $SCR_{NO}$ , Fig. 14b), below the light-off temperature (ca. 350 °C), besides  $Rh$ -nitrosyls, a large amount of nitrites/nitrates appeared in the spectra (1615–1560  $cm^{-1}$  region) originating from the  $NO_2$  formed in the gas phase. The nitrites/nitrates species probably hindered the formation of formaldehyde-like species and, therefore, hampered the  $CH_4$  activation. On the other hand, as the light-off temperature was approached, the intensity of the  $Rh$ -nitrosyls and nitrites/nitrates bands decreased and the band of carbonyls (at ca. 2020 and 1910  $cm^{-1}$ ) appeared in the spectrum together with the band of the formaldehyde-like species at 1625  $cm^{-1}$ , indicating that  $CH_4$  activation started to occur.

### 3.5.4. Surface species during NO and $N_2O$ simultaneous reduction with $CH_4$ in the presence of $O_2$

When  $N_2O$  and  $NO$  were co-fed with  $CH_4$  and  $O_2$  ( $SCR_{sim}$ ), the light-off temperature for  $NO$  and  $N_2O$  conversion was the same, ca. 400 °C (inset in Fig. 15). It should be noted that the light-off temperature shifted to higher temperature if compared to the values found for the separate abatement reactions (ca. 350 °C for  $SCR_{NO}$  and ca. 300 °C for  $SCR_{N_2O}$ , see insets of Figs. 13b and 14b). This can be explained by taking into account that below the light-off temperature, besides a low amount of  $Rh$ -nitrosyls (bands at ca. 1800 and 1915  $cm^{-1}$ ), a rather large amount of nitrites/nitrates species (1615–1560  $cm^{-1}$  region) was observed, as in  $SCR_{NO}$  (Fig. 15). Such nitrites/nitrates species could be responsible for the poisoning of active sites, by blocking the surface species reactive for  $CH_4$ ,  $NO$  or  $N_2O$  activation (vide supra). This is supported by the evidence that, at the light-off temperature, the intensity of nitrites/nitrates



**Fig. 15.** Operando-FTIR spectra of surface species and (inset a) the corresponding catalytic results (NO,  $N_2O$  and  $CH_4$  conversion and  $CO_2$  selectivity) during  $SCR_{sim}$  at increasing temperature from 200 to 500 °C (stepwise 25 °C) on activated Pt,Pd,Rh/ $TiO_2$ -Zr $O_2$  catalyst. Reactants concentration:  $[N_2O]=[NO]=[CH_4]=4000$  ppm,  $[O_2]=2500$  ppm (total flow rate=100  $cm^3$  STP/min, He as balance). The magnification of the  $\nu_{NH}$  region is reported in the inset b.



bands remarkably decreased, likely due to their desorption, thus leaving the surface noble metal oxide species free to react. The larger shift observed for N<sub>2</sub>O conversion light-off temperature is likely due to the competition of strongly adsorbed nitrite/nitrate species for the N<sub>2</sub>O adsorption sites. A concomitant phenomenon likely causing the shift of the light-off to higher temperature can be the large amount of oxidants (N<sub>2</sub>O, NO and O<sub>2</sub>) which are preventing the reduction of the noble metal oxide surface species responsible in the reduced state for the CH<sub>4</sub> and NO activation. Moreover, approaching the light-off temperature, bands of formaldehyde-like species and formates (1630 and 1540 cm<sup>-1</sup>, respectively) and, although of low intensity, of carbonyls appeared in the spectra, indicating that the CH<sub>4</sub> activation is starting, while the Rh-nitrosyl bands interconversion occurred, as already observed in the SCR<sub>NO</sub>. Interestingly, the weak band of ν<sub>NH</sub> (3230 cm<sup>-1</sup> [63]) is appearing and its intensity remained fairly constant also at temperatures higher than the light-off value. Such a weak band, not found in the CR<sub>NO</sub> and SCR<sub>NO</sub> reactions but observed in the CR<sub>N2O</sub> and SCR<sub>N2O</sub> reactions above the light-off temperature, suggests a pathway in the SCR<sub>sim</sub> in which the dissociative chemisorption of CH<sub>4</sub> and N<sub>2</sub>O is supplying the N and H species necessary to form NH<sub>3</sub>. This would imply the breaking of the C-H and of the N-N bonds on the noble metal sites.

As a whole, according to all the experimental findings, taking into account the high complexity of the SCR<sub>sim</sub> process as well as of the catalysts on which it occurs, some considerations about the active sites and the possible pathway of NO and N<sub>2</sub>O abatement can be suggested.

The abatement of NO and N<sub>2</sub>O is occurring on two different active sites formed along the reaction.

The surface of noble metal oxide-like species are easily reduced by CH<sub>4</sub> to metals or partly reduced Me-MeO<sub>x</sub> interfaces, as supported by the formation of CH<sub>x</sub>O<sub>y</sub> adsorbed species. On the surface of reduced noble metal particles, the CH<sub>4</sub> activation occurs through the decomposition into C and H adsorbed atoms. Such a decomposition is supported by the adsorbed very tiny amount of NH<sub>3</sub> formed above the light-off temperature requiring H atoms coming from the homolytic CH<sub>4</sub> dissociation. Moreover, the NO activation also occurs on the CH<sub>4</sub> reduced noble metal particles. This is enabling the NO dissociative adsorption into N and O adsorbed atoms, which can react with the CH<sub>4</sub>-deriving C and H adsorbed species formed on adjacent noble metal sites. This last reaction step is supported by the formation of adsorbed carbonyls at the light-off of all NO-involving reactions.

The N<sub>2</sub>O activation occurred on noble metal sites, as either surface cations or Me-MeO<sub>x</sub> interfaces, having redox ability that is enhanced by CH<sub>4</sub>. The reactive oxygen species coming from the N<sub>2</sub>O decomposition step can be responsible for the CH<sub>4</sub> oxidative dehydrogenation to give formaldehyde-like species which will lead to CO and CO<sub>2</sub> possibly *via* surface carbonyls intermediates.

The presence of O<sub>2</sub> in the reactant stream has an inhibiting effect on the SCR<sub>sim</sub> activity mainly for two reasons. First, O<sub>2</sub> can oxidise the reduced or partly reduced metal surface, thus inhibiting the formation of the sites active for NO and CH<sub>4</sub> or N<sub>2</sub>O activation. The second reason is that O<sub>2</sub> reacts with gaseous NO yielding NO<sub>2</sub> which give rise to adsorbed nitrates intermediates poisoning the active sites at lower temperatures. On the other hand, as a positive effect, the presence of O<sub>2</sub> is essential for guaranteeing a complete selectivity to CO<sub>2</sub> thus avoiding the undesired CO formation. Therefore, for practical application it is necessary to balance adequately the amount of O<sub>2</sub> in the exhaust stream.

#### 4. Conclusions

The simultaneous abatement of NO and N<sub>2</sub>O with CH<sub>4</sub> in the presence of O<sub>2</sub> (SCR<sub>sim</sub>) on both Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub> and Pt,Pd,Rh/TiO<sub>2</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts strongly depends on the O<sub>2</sub>/CH<sub>4</sub> feed ratio. Indeed, the best catalytic performance is obtained when the O<sub>2</sub>/CH<sub>4</sub> ratio is less than 1 (O<sub>2</sub>/CH<sub>4</sub> = 2500/4000 v/v). In such conditions, above 400°C, CH<sub>4</sub> efficiently and simultaneously reduces NO and N<sub>2</sub>O with negligible formation of by-products when O<sub>2</sub> is almost completely consumed by

combustion. As the O<sub>2</sub>/CH<sub>4</sub> ratio is higher than 1 (O<sub>2</sub>/CH<sub>4</sub> = 5000/4000 or 10000/4000 v/v), the SCR<sub>sim</sub> becomes ineffective as the NO conversion is negligible due to CH<sub>4</sub> combustion which becomes the prevailing reaction. However, the presence of O<sub>2</sub> in the reactant stream is necessary to guarantee a good CO<sub>2</sub> selectivity.

Two different active sites, formed along the SCR<sub>sim</sub> reaction, are suggested to be responsible for the NO and N<sub>2</sub>O abatement with CH<sub>4</sub> and O<sub>2</sub> in the mixture in the adequate ratio. Noble-metal sites in the reduced state activate the decomposition of CH<sub>4</sub> and NO, while those partly reduced activate N<sub>2</sub>O dissociation into N<sub>2</sub> and surface O-species. The role of CH<sub>4</sub> in the pathway is crucial as it likely removes reactive O-species from the surface of noble-metal oxide-like nanoparticles. The content of O<sub>2</sub> is critical for the catalyst surface redox properties because it hinders CH<sub>4</sub> in ensuring the formation of reduced or partly reduced noble-metal species that are acting as catalytic reactive centers. The *operando* FT-IR findings support this pathway view: (i) adsorbed CH<sub>x</sub>O<sub>y</sub> species, observed below the light-off temperature, indicate that the reduction of noble metal oxide surface occurs by stepwise CH<sub>4</sub> oxidative dehydrogenation; (ii) the adsorbed NH<sub>3</sub>, observed above the light-off temperature, supports the homolytic CH<sub>4</sub> and N<sub>2</sub>O (and/or NO) dissociation on the reduced noble metals surface; (iii) the formaldehyde-like and carbonyls species, formed at the light-off temperature, suggest that they likely are reaction intermediates; (iv) strongly adsorbed nitrite/nitrate species, arising from O<sub>2</sub> reacting with NO, account for the poisoning of active sites, blocking reactive O-species on the noble-metal oxide surface.

As the noble metal oxide-like nanoparticles are characterized by a different reducibility (Pd ≥ Pt >> Rh), along SCR<sub>sim</sub> process, PdO<sub>x</sub> and PtO<sub>x</sub> oxide-like species are suggested to be more easily reduced by CH<sub>4</sub> at the surface, forming surface metal sites or Pd-PdO<sub>x</sub> and Pt-PtO<sub>x</sub> interfaces, while Rh<sub>x</sub>O<sub>y</sub>-like species appear to be less reducible, as indicated by Rh-NO/Rh-NO<sup>+</sup> species interconversion under reaction conditions.

The reduction/oxidation process of the surface noble-metal species responsible for the reactants activation is affected by the interaction with the support. Indeed, this is confirmed by the presence of CeO<sub>2</sub> that, even in a small amount, is improving the catalyst redox properties, through an increase of the surface O-mobility.

Finally, an assay of the catalytic behaviour in the presence of water revealed that the active sites were also preserved under these conditions, leading to a catalytic activity even slightly better than that found in the absence of water. Such evidence makes this catalysts system promising for a possible application of simultaneous abatement of NO and N<sub>2</sub>O with CH<sub>4</sub> under the real conditions.

#### CRedit authorship contribution statement

**Maria Cristina Campa:** Conceptualization, Methodology, Supervision, Investigation, Data curation, Writing – original draft, Writing – review & editing. **Giuseppe Fierro:** Conceptualization, Formal analysis, Writing – original draft, Writing – review & editing. **Aidan M. Doyle:** Resources, Investigation, Writing – original draft. **Simonetta Tuti:** Investigation, Formal analysis. **Carlotta Catracchia:** Investigation, Data curation, Formal analysis. **Daniela Pietrogiamomi:** Conceptualization, Methodology, Supervision, Investigation, Data curation, Resources, Writing – original draft, Writing – review & editing, Funding acquisition.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

## Acknowledgments

We gratefully acknowledge ‘Sapienza’ University of Rome for financial support (Research Project 2016 - Grant n. RG116154E1F7B680), Dr. Sara Passeri for contributing to *Operando*-FTIR data collections and Dr. Simona Marta (BASF Italia S.p.A., Rome) for chemical analysis.

## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.surfin.2023.103502.

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