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## On the promotional effect of Pd on the propene-assisted decomposition of NO on chlorinated Ce<sub>0.68</sub> Zr<sub>0.32</sub> O<sub>2</sub>

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2 **On the promotional effect of Pd**  
3 **on the propene-assisted decomposition of NO**  
4 **on chlorinated Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub>**

5  
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15  
16 **Running title:** C<sub>3</sub>H<sub>6</sub>-assisted decomposition of NO on PdO<sub>x</sub>/Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> catalysts

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1 **Abstract:**

2           The Selective Catalytic Reduction (SCR) of NO<sub>x</sub> assisted by propene is investigated  
3 on Pd/Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> catalysts (Pd/CZ), and is compared, under identical experimental  
4 conditions, with that found on a Pd/SiO<sub>2</sub> reference catalyst. Physico-chemical characterisation  
5 of the studied catalysts along with their catalytic properties indicate that Pd is not fully  
6 reduced to metallic Pd for the Pd/CZ catalysts. This study shows that the incorporation of Pd  
7 to CZ greatly promotes the reduction of NO in the presence of C<sub>3</sub>H<sub>6</sub>. These catalysts display  
8 very stable deNO<sub>x</sub> activity even in the presence of 1.7% water, the addition of which induces  
9 a reversible deactivation of about 10%. The much higher N<sub>2</sub> selectivity obtained on Pd/CZ  
10 suggests that the lean deNO<sub>x</sub> mechanism occurring on these catalysts is different from that  
11 occurring on Pd<sup>0</sup>/SiO<sub>2</sub>. A detailed mechanism is proposed for which CZ achieves both NO  
12 oxidation to NO<sub>2</sub> and NO decomposition to N<sub>2</sub>, whereas PdO<sub>x</sub> activates C<sub>3</sub>H<sub>6</sub> via ad-NO<sub>2</sub>  
13 species, intermediately producing R-NO<sub>x</sub> compounds that further decompose to NO and  
14 C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>. The role of the latter oxygenates is to reduce CZ to provide the catalytic sites  
15 responsible for NO decomposition. The proposed C<sub>3</sub>H<sub>6</sub>-assisted NO decomposition  
16 mechanism stresses the key role of NO<sub>2</sub>, R-NO<sub>x</sub> and C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> as intermediates of the SCR of  
17 NO<sub>x</sub> by hydrocarbons.

18

19

20 **Key Words:** CO-FTIR, XANES, Lean deNO<sub>x</sub>, Mechanism, C<sub>3</sub>H<sub>6</sub>, Pd catalysts, Ceria-  
21 Zirconia, TPD of NO<sub>x</sub>

22

## 1 **1. Introduction**

2 A tremendous number of investigations have been made within the past decades to  
3 develop catalysts capable of decreasing the emissions of air pollutants such as carbon  
4 monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO<sub>x</sub>) from automotive gas exhausts  
5 [1-6]. The development of improved catalysts to meet the ever more stringent emissions  
6 standards is, however, still of key importance. To achieve this goal, the most promising means  
7 would obviously be to find a catalytic system that could directly decompose NO over a wide  
8 range of temperatures as pointed out by Pârvulescu et al. in a rather recent review [4].  
9 Although a large number of catalysts have already been tested, no such system has as yet been  
10 found.

11 Three-Way Catalysts (TWC) were among the first possibilities investigated for lean  
12 NO<sub>x</sub> abatement in car exhausts. These catalysts, which typically operate with an air-to-fuel  
13 ratio (A/F) close to the stoichiometry [1,5-7], are generally made up of a quite complicated  
14 combination of noble metals supported on an oxide carrier. These noble metals have shown to  
15 dissociate readily NO when present in their fully reduced state [1,2,4,8-10].

16 In addition to the ever more restricting limitations on carbon monoxide and nitrogen  
17 oxides, new regulations have appeared concerning the emission of carbon dioxide which is  
18 well known to be one of the greenhouse gases responsible for global warming. From this  
19 point of view, diesel engines, which operate typically under a lean mixture (air-to-fuel ratio  
20 (A/F) greater than unity), is among the solutions that must be considered to meet the CO<sub>2</sub>  
21 emission requirements. Indeed, such burning conditions lead to a lowering of fuel  
22 consumption and consequently to a decrease of the CO<sub>2</sub> emissions. Although these lean  
23 conditions have solved essentially the carbon monoxide and unburned hydrocarbon emission  
24 problems, they have made the classic TWC ineffective in removing nitrogen oxides from lean  
25 automotive gas exhausts.

1           The catalytic solution using a traditional TWC associated with a storage component  
2 (barium carbonate: BaCO<sub>3</sub>) [11] which has been adopted for lean gasoline engines has still to  
3 be adapted for diesel cars which, as yet, have no suitable catalytic solution. A more attractive  
4 alternative would be to develop a specific catalyst capable of reducing nitrogen oxide  
5 emissions under lean conditions.

6           Among all the different formulations evaluated, to date, zeolite-based catalysts are  
7 probably those which have been studied most [3,4]. This might be due to the promising  
8 findings of Iwamoto et al. [12,13] and Lee and Armor [14] who showed that Cu-exchanged  
9 ZSM5 is able to decompose nitrogen monoxide at RT. This decomposition process is,  
10 however, self-inhibiting since as soon as nitrogen monoxide is decomposed on the catalytic  
11 sites (copper ions) they are poisoned by the oxygen left from nitrogen monoxide  
12 decomposition and, thus, the reaction stops. It is important to notice the striking similarity  
13 with model TWC reported in the case of stoichiometric mixture by Djéga-Mariadassou and  
14 co-workers [7,15,16]. These authors demonstrated the competition between the CO oxidation  
15 reaction and the assisted decomposition of NO by CO. In lean exhausts, carbon monoxide  
16 cannot be further used to assist the decomposition of nitrogen monoxide [16]. Consequently,  
17 other reductants such as hydrocarbons must be used to assist the decomposition of nitrogen  
18 monoxide. In the case of model exhausts, it has been shown by Matsumoto et al. [17] that  
19 alkenes, and more particularly propene, are the most efficient reductants to assist the nitrogen  
20 monoxide reduction. Alkenes are, however, also known as coke precursors for acidic catalysts  
21 which accounts for the dramatic deactivation of zeolite-based catalysts when propene is  
22 present in the lean mixture [18]. In addition to this coking phenomenon, zeolite-based  
23 catalysts are rather sensitive to water, and deactivation was also reported due to their low  
24 hydrothermal resistance [4]. These drawbacks have led researchers to focus on oxides-  
25 supported Platinum Group Metals (PGMs) catalysts. Due to their intrinsic higher activity [19-

1 21], supported Pt catalysts have been the subject of the greatest number of studies [9,22-33].  
2 These are followed by supported Rh [10,19-21,33] and Pd [19-21,33,34] catalysts. Although  
3 these catalysts exhibit significant lean deNO<sub>x</sub> activity with C<sub>3</sub>H<sub>6</sub> as reductant and quite  
4 reasonable stability, they have a rather narrow temperature operating window [19] and fairly  
5 poor selectivity to N<sub>2</sub> [9,30,34,35]. N<sub>2</sub>O, which is well known as a component of the  
6 greenhouse effect [36], is, indeed, formed in substantial amounts. High selectivity to N<sub>2</sub> has,  
7 however, been reported for Rh/Al<sub>2</sub>O<sub>3</sub> catalysts [10,19,33]. Alumina-supported Rh catalysts  
8 usually operate at much higher temperatures than either supported Pt or Pd catalysts. This  
9 peculiarity led Obuchi et al. to the conclusion that this high selectivity to N<sub>2</sub> was attributable  
10 to an additional catalytic effect of the alumina support [33]. The influence of the nature of the  
11 support was also investigated [19,20,30]. These studies, however, did not report on PGMs  
12 supported on ceria-zirconia (CZ) until recently for Rh/CZ [37] or Pt catalysts supported on  
13 CZ-Al<sub>2</sub>O<sub>3</sub> [31] and pure CZ [32]. Finally, CZ showed only very moderate lean deNO<sub>x</sub> activity  
14 in the presence of C<sub>3</sub>H<sub>6</sub> [38].

15 The aim of this work is to investigate the influence of Pd addition to a chlorinated  
16 ceria-zirconia support on lean deNO<sub>x</sub> with C<sub>3</sub>H<sub>6</sub> as reductant. To our knowledge, such  
17 catalysts have not been investigated for this particular reaction. They have, however, been  
18 widely studied in the fields of TWC [39-43], CH<sub>4</sub> total oxidation [44,45] and hydrocarbon  
19 reforming [46]. For comparison, the performances of a Pd/SiO<sub>2</sub> catalyst are also reported.  
20 Pd/CZ catalysts show enhanced lean deNO<sub>x</sub> activity and much higher N<sub>2</sub> selectivity compared  
21 to Pd/SiO<sub>2</sub>. This suggests the involvement of distinct lean deNO<sub>x</sub> reaction mechanisms within  
22 these two catalytic systems. Based on transient and steady-state experiments, a mechanism of  
23 the lean deNO<sub>x</sub> is proposed for the Pd/CZ catalysts.

24

25

## 1 **2. Experimental**

2

### 3 *2.1. Catalyst synthesis*

#### 4 *2.1.1. Ceria-zirconia ( $Ce_{0.68}Zr_{0.32}O_2$ : CZ)*

5 The CZ solid solution was provided by Rhodia. The CZ was added to chloridric acid  
6 solution (pH 1.9) prepared by adding HCl to distilled water. After ageing for 2 hours under  
7 vigorous stirring, CZ was filtered and washed with distilled water before being dried in air at  
8 120°C for 3 hours.

9

#### 10 *2.1.2. Pd/CZ*

11 Two ceria-zirconia-supported Pd catalysts (0.54 and 0.89 wt% Pd) were prepared by  
12 incipient wetness impregnation of the chlorinated support by an aqueous solution of PdCl<sub>2</sub>,  
13 3H<sub>2</sub>O (Johnson Matthey). After impregnation, the catalysts were aged for 2 hours and dried in  
14 air at 120°C for three hours.

15

#### 16 *2.1.3. Pd/SiO<sub>2</sub>*

17 For comparison with Pd/CZ catalysts, a silica (Degussa, Aerosil 50)-supported  
18 palladium catalyst (0.93 wt% Pd) was prepared by incipient wetness impregnation of the  
19 support by an aqueous solution of PdCl<sub>2</sub>, 3 H<sub>2</sub>O (Johnson Matthey). After impregnation, the  
20 catalyst was aged for 2 hours and dried in air at 120°C for three hours.

21

### 22 *2.2. Catalyst characterization*

23 Metal and chlorine contents were determined by chemical analyses (CNRS –  
24 Vernaison). The chlorine content was about 1 wt% for the CZ-based catalysts before and after  
25 reaction.

1           The specific surface areas were determined by physisorption of N<sub>2</sub> at 77K using a  
2 Quantasorb Jr. dynamic system equipped with a thermal conductivity detector (TCD). The  
3 specific surface areas were calculated using the BET method. For CZ-supported catalysts, the  
4 specific surface areas were about 100 m<sup>2</sup> g<sup>-1</sup> before and after testing, whereas that of Pd/SiO<sub>2</sub>  
5 was about 50 m<sup>2</sup> g<sup>-1</sup>.

### 7 *2.2.1 Determination of the percentage of exposed zero-valent Pd atom (PEM<sup>0</sup>)*

8           With the well-known reducibility of the CZ support [47], the determination of the  
9 percentage of exposed zero-valent Pd atom was done by means of propene hydrogenation  
10 [48].

11           Prior to propene hydrogenation, the catalyst sample (30-60 mg deposited on sintered  
12 glass of a pyrex reactor) was heated in flowing H<sub>2</sub> (100 mL<sub>NTP</sub> min<sup>-1</sup>) at atmospheric pressure  
13 with a heating rate of 3°C min<sup>-1</sup> up to 300°C and was kept at this temperature for 2h. After  
14 cooling to -78°C under H<sub>2</sub>, the reaction was started. The partial pressure of propene was 51.8  
15 torr, and the total flow rate was 107 mL<sub>NTP</sub> min<sup>-1</sup> with H<sub>2</sub> as balance.

16           The composition of the effluents was analyzed by means of an on-line gas  
17 chromatograph (Hewlett Packard 5890, FID) equipped with a CP-Al<sub>2</sub>O<sub>3</sub>/KCl (Chrompack,  
18 50 m long, 0.32 mm inner diameter, 5 µm film thickness) capillary column. The only detected  
19 product was propane.

20           From the initial reaction rates obtained, the numbers of exposed zero-valent Pd atoms  
21 were calculated according to a turnover rate of 0.40 s<sup>-1</sup> for the propene hydrogenation reaction  
22 at -78°C [48].

### 1 2.2.2. *Temperature-Programmed Reduction*

2 Temperature-Programmed Reduction (TPR) experiments were performed in a  
3 conventional system equipped with a thermal conductivity detector. After calcination at  
4 500°C for 2h, the reduction was carried out in a flow of H<sub>2</sub> (5%) in Ar (25 mL min<sup>-1</sup>) using a  
5 heating rate of 5°C min<sup>-1</sup>. Typically, the reduction was carried out up to 700°C and then the  
6 sample (0.02-0.05 g) was kept at this temperature for 15 min. H<sub>2</sub>O evolving in the course of  
7 the TPR experiments was trapped by a 5A molecular sieve. The amount of H<sub>2</sub> uptake in the  
8 TPR was estimated from integrated peak areas.

9

### 10 2.2.3. *X-Ray diffraction*

11 X-Ray diffraction (XRD) patterns of CZ, SiO<sub>2</sub>, Pd(0.93)/SiO<sub>2</sub> and Pd/CZ were  
12 obtained on a SIEMENS D500 diffractometer with a Cu K<sub>α</sub> monochromatized radiation.

13

### 14 2.2.4. *X-ray absorption near edge spectroscopy (XANES)*

15 X-Ray absorption measurements were carried out using synchrotron radiation of the  
16 XAS13 station at LURE (Orsay, France) on line D42 (May 3-4, 2001). Fluorescence yield  
17 spectra of Pd(0.54)/CZ were recorded at RT using a Ge solid detector (Eurisyss, 7 elements)  
18 combined with a multichannel analyser to select the Pd K<sub>α</sub> fluorescence, whereas those of the  
19 reference compounds (Pd foils, 20 μm thick, PdO (> 99% pure, Lancaster)) were collected in  
20 the transmission mode. The incident beam was monochromatized using a Ge (400) double  
21 monochromator. XANES spectra were collected at the Pd K edge with a sampling step of 2.0  
22 eV/point from 24300 to 24500 eV and an integration time of 10s and 2s in fluorescence and  
23 transmission modes, respectively. The energy was calibrated using the Pd foil. XANES  
24 spectra were obtained from Pd(0.54)/CZ either after oxidation or reduction treatments under  
25 flowing air or H<sub>2</sub> (100 mL<sub>NTP</sub> min<sup>-1</sup>) for 2h at 500°C. To avoid the exposure of the reduced

1 sample to O<sub>2</sub>, the catalyst was then transferred into a UV cell (Suprasil quartz, 5 cm long, 1 cm  
2 wide and 1 cm high) that was finally sealed under vacuum ( $5 \times 10^{-5}$  torr). In the case of the  
3 oxidized sample, we checked that the high purity silica glass did not interfere with incident  
4 and fluorescent beams. Superimposed spectra were, indeed, obtained with this sample located  
5 either into the UV cell or between Kapton tapes. The cell was set to 45° with respect to the  
6 incident RX beam and the fluorescence detector. The extraction of the data was done with  
7 Michalowicz's software package [49,50].

8

#### 9 *2.2.5. Fourier transform infra-red spectroscopy*

10 Fourier transform infra-red (FTIR) spectra of adsorbed CO on CZ and Pd(0.89)/CZ  
11 were collected on a Bruker Vector 22 FTIR spectrometer equipped with a liquid N<sub>2</sub>-cooled  
12 MCT detector and a data acquisition station. 256 scans were averaged with a spectral  
13 resolution of 2 cm<sup>-1</sup>.

14 The samples were pressed into self-supporting wafers of 6-11 mg cm<sup>-2</sup>. The wafers  
15 were loaded in a moveable glass sample holder, equipped on top with an iron magnet, inserted  
16 in a conventional pyrex-glass cell (CaF<sub>2</sub> windows) connected to a vacuum system. The iron  
17 magnet allowed the transfer of the catalyst sample from the oven-heated region to the infrared  
18 light beam.

19 Prior to adsorption of CO, the catalysts were submitted to a dynamic (50 cm<sup>3</sup> min<sup>-1</sup>)  
20 reducing pretreatment (5% H<sub>2</sub> in Ar, Air Liquide, 99.999%) at 500°C for 2 h at atmospheric  
21 pressure. The catalyst samples were then evacuated (10<sup>-6</sup> mbar) at 500°C for 60 min before  
22 the temperature was decreased to RT under dynamic vacuum.

23 CO (Air Liquide, 99.999%), trapped at 77 K, was adsorbed at RT at equilibrated  
24 pressures of 0.9 and 18 torr.

1           The spectrum of the pretreated catalyst was used as reference and subtracted from the  
2 spectra of the catalyst exposed to CO.

3

### 4 *2.3. Catalytic runs*

5           Prior to catalytic runs, the samples were calcined in situ in dry air at 500°C  
6 (4°C.min<sup>-1</sup>) for 2 hours with a flow rate of 500 mL<sub>NTP</sub> min<sup>-1</sup> per gram of catalyst.

7           Steady-state, Temperature-Programmed Desorption (TPD) and Temperature-  
8 Programmed Surface Reaction (TPSR) experiments and were carried out. After being  
9 contacted with the appropriate gas mixture at RT, temperature transient experiments were  
10 carried out from RT to 500°C with a heating rate of 10°C min<sup>-1</sup>. Before the TPD experiments,  
11 the catalyst samples were flushed in N<sub>2</sub> to remove RT physisorbed species from the  
12 adsorption mixture.

13           The experiments were carried out in a U-type quartz reactor. The sample (0.2 g unless  
14 otherwise specified) was held between plugs of quartz wool, and the temperature was  
15 controlled through a WEST 4000 temperature controller using a K type thermocouple.  
16 Reactant gases were fed from independent mass flow controllers (Brooks 5850E). The total  
17 flow was 250 mL<sub>NTP</sub> min<sup>-1</sup> to which corresponds a HSV (Hour Space Velocity) of  
18 112,500 h<sup>-1</sup>.

19           Catalytic experiments were carried out with C<sub>3</sub>H<sub>6</sub> as reductant. Typically, the  
20 composition of the C<sub>3</sub>H<sub>6</sub>-NO-O<sub>2</sub> reacting mixture was: 1900 ppm C<sub>3</sub>H<sub>6</sub>, 340 ppm NO and 8%  
21 O<sub>2</sub> in N<sub>2</sub>. The reactants, diluted in N<sub>2</sub>, were fed from independent gas cylinders (Air Liquide).

22           The reactor outflow was continuously analysed using the combination of four different  
23 detectors. An Eco Physics CLD 700 AL chemiluminescence NO<sub>x</sub> analyser (for NO and total  
24 NO<sub>x</sub> (*i.e.* NO + NO<sub>2</sub>)) allowed the simultaneous detection of both NO and NO<sub>x</sub>. Two Ultramat  
25 6 IR analysers were used to monitor N<sub>2</sub>O, CO and CO<sub>2</sub>. A FID detector (Fidamat 5A) was

1 used to follow the concentration of hydrocarbons. We checked that, under our experimental  
 2 conditions, CO and CO<sub>2</sub> had a negligible response on the N<sub>2</sub>O IR analyser, whereas that of  
 3 C<sub>3</sub>H<sub>6</sub> was significant. C<sub>3</sub>H<sub>6</sub> contribution to the N<sub>2</sub>O signal was taken into account to calculate  
 4 the "true" N<sub>2</sub>O concentration ([N<sub>2</sub>O]) as follows (Eq. 1):

$$5 \quad [N_2O] = [N_2O]_{\text{meas.}} - \frac{[N_2O]^0 \times [C_3H_6]_{\text{meas.}}}{[C_3H_6]_{\text{inlet}}} \quad (1)$$

6 where [N<sub>2</sub>O]<sup>0</sup>, [C<sub>3</sub>H<sub>6</sub>]<sub>inlet</sub>, [C<sub>3</sub>H<sub>6</sub>]<sub>meas.</sub> and [N<sub>2</sub>O]<sub>meas.</sub> are: the concentrations of N<sub>2</sub>O due to the  
 7 contribution of the inlet concentration of C<sub>3</sub>H<sub>6</sub>, the inlet concentration of C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub> and N<sub>2</sub>O  
 8 concentrations measured in the course of the reaction, respectively. As N<sub>2</sub> was used as  
 9 balance, the conversion of NO<sub>x</sub> to N<sub>2</sub> was calculated assuming 100% nitrogen mass balance  
 10 (Eq. 2):

$$11 \quad \text{Conversion of NO}_x \text{ to N}_2 \text{ (\%)} = \frac{[NO_x]_{\text{inlet}} - ([NO_x]_{\text{outlet}} + 2 \times [N_2O])}{[NO_x]_{\text{inlet}}} \quad (2)$$

12 where [NO<sub>x</sub>]<sub>inlet</sub> and [NO<sub>x</sub>]<sub>outlet</sub> are the concentrations of NO<sub>x</sub> at the inlet and at the outlet of  
 13 the reactor, respectively.

14 In one experiment, over Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub>, propene was substituted by 1-propanol (Merck,  
 15 spectroscopic grade) with a concentration of 2200 ppm by means of a saturator.

16

### 17 **3. Results**

18

#### 19 *3.1. Catalyst characterization*

##### 20 *3.1.1. Determination of the percentage of exposed zero-valent metal atoms (PEM<sup>0</sup>)*

21 Table 1 lists the percentage of exposed zero-valent palladium atoms of the CZ-  
 22 supported Pd catalysts and Pd(0.93)/SiO<sub>2</sub>. The percentage of exposed zero-valent Pd atoms is  
 23 about 17 and 22% for Pd/CZ and Pd(0.93)/SiO<sub>2</sub>, respectively.

### 1 3.1.2. TPR results

2 Fig. 1 shows the TPR profiles of the calcined catalysts. For Pd(0.93)/SiO<sub>2</sub>, the trace of  
3 which is magnified by a factor of 4 for the sake of clarity, a reduction peak is observed at  
4 about 50°C.

5 For the CZ sample, the trace of which is magnified by a factor of 3, a broad reduction  
6 peak starting around 400°C and ranging to a maximum at 530°C is observed. This reduction  
7 temperature region corresponds well with that reported for various ceria-zirconia materials  
8 [51-55].

9 The presence of noble metal on CZ modifies substantially the features of the TPD  
10 profiles. Indeed, the reduction peak revealed over the CZ sample vanishes, while a strong  
11 signal appears at temperatures below 200°C depending on the catalyst sample. It is observed  
12 that the reduction peak shifts to lower temperature with increasing Pd content. Luo and Zheng  
13 [56] reported a similar feature despite the fact that their TPR traces were substantially  
14 different from ours.

15 As it is well established that the incorporation of noble metals increases the  
16 reducibility of the ceria-related materials [47,51,52,56,57], quantitative analysis of the TPR  
17 traces is not discussed. Overall, the amount of H<sub>2</sub> consumed in the course of the TPR was  
18 close to 0.5 10<sup>-3</sup> mol g<sup>-1</sup> for all samples. This value agrees well with those listed by Luo and  
19 Zheng for Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>-supported Pd catalysts [56].

20 Finally, the comparison of the TPR traces of Pd(0.93)/SiO<sub>2</sub> and Pd(0.89)/CZ clearly  
21 shows that the Pd species interact to a greater extent with CZ than with SiO<sub>2</sub>. The reduction  
22 peak of these Pd species supported on CZ is, indeed, shifted to higher temperature compared  
23 with that of Pd(0.93)/SiO<sub>2</sub>.

24

25

### 1 3.1.3. XRD

2 XRD patterns of the calcined SiO<sub>2</sub>, Pd(0.93)/SiO<sub>2</sub> and CZ samples are shown in Fig. 2.  
3 After calcination of Pd(0.93)/SiO<sub>2</sub>, a diffraction peak is observed at about 33.8° which  
4 corresponds to PdO (101 plane). Two very weak peaks at about 41.9 and 54.8° can also be  
5 assigned to PdO. As shown in Fig. 2, the diffraction pattern of CZ exhibits 4 peaks at about  
6 29, 33.8, 48.3 and 57.2°. Owing to the weak intensity of the PdO peaks and the overlapping  
7 with CZ support, the presence of PdO on the CZ-supported catalysts could not be established  
8 through XRD.

9

### 10 3.1.4. XANES measurements

11 XANES spectra of the Pd(0.54) catalyst after calcination or reduction are shown in  
12 Fig. 3. The shape of the XANES spectra of the Pd(0.54)/CZ sample either calcined (----) or  
13 reduced (—) corresponds fairly well to that of the PdO (▲) and Pd metal (Δ) references (Fig.  
14 3), respectively. This result markedly differs from that of the reduced Rh/CZ catalyst, which  
15 showed a XANES spectrum different from both Rh foil and Rh<sub>2</sub>O<sub>3</sub> references [58].

16

### 17 3.1.5. IR

18 The CO-FTIR technique was used to probe the nature of the metal species [59]  
19 supported on CZ.

20 The FTIR spectra of adsorbed CO under equilibrated pressures of 0.9 and 18 torr of  
21 CO are shown in Fig. 4 for CZ and Pd(0.89)/CZ. It is worthwhile noting the fairly low  
22 intensity of the CO absorption bands. This is why the CO-FTIR of the Pd(0.54)/CZ catalyst  
23 was not investigated.

24 Over CZ (Fig. 4a), two CO absorption bands are observed at 1575 and 2167 cm<sup>-1</sup>. The  
25 band at 1575 cm<sup>-1</sup> can be assigned to the formation of carbonates [60]. This band appears as

1 soon as the equilibrated pressure of CO is 0.9 torr, whereas the band at  $2167\text{ cm}^{-1}$  is observed  
2 only at a pressure of 18 torr. This latter band has been attributed to the weak interaction of CO  
3 with Ce surface sites [61-64].

4 The FTIR spectra of adsorbed CO on Pd(0.89)/CZ (Fig. 4b) differ markedly from  
5 those of CZ. The formation of carbonate is not observed, and a rather broad absorption band  
6 from  $1850$  to  $2090\text{ cm}^{-1}$  is revealed, with two maxima at  $1950$  and  $2083\text{ cm}^{-1}$ . The band at  
7  $1950\text{ cm}^{-1}$ , also found in a previous work of Badri et al. on a chlorinated Pd/CeO<sub>2</sub> sample  
8 [61], can be assigned to bridged CO species bonded to zero-valent Pd atoms (Pd<sup>0</sup><sub>2</sub>CO)  
9 [43,65,66]. In contrast, the band with the maximum at  $2083\text{ cm}^{-1}$  corresponds to CO species  
10 singly bonded to Pd<sup>0</sup> atoms [43,59,61,63,65]. CO coordinated to Ce<sup>Z+</sup> centers, acting as Lewis  
11 acid sites, gives rise to an absorption band at  $2175\text{ cm}^{-1}$ , as already reported by Badri et al.  
12 [61].

13

#### 14 3.1.6. NO oxidation

15 As reported earlier [38 and references therein], the oxidation of NO to NO<sub>2</sub> is  
16 suspected to be an essential step of the deNO<sub>x</sub> process. This reaction was, thus, investigated  
17 over CZ and Pd(0.54)/CZ under steady-state conditions. As shown in Fig. 5, NO oxidation is  
18 the greatest at 400°C. At higher temperatures, the conversion of NO decreases due to  
19 thermodynamic limitations. It is important to note that the addition of Pd does not promote  
20 NO oxidation, and this reaction is only catalysed by the CZ support.

21

#### 22 3.1.7. Adsorption of NO-O<sub>2</sub> – TPD in N<sub>2</sub>

23 Fig. 6 shows the NO<sub>x</sub> TPD profiles in N<sub>2</sub> of samples contacted with NO-O<sub>2</sub> (340 ppm-  
24 8%). The addition of Pd to CZ does not affect the TPD profiles to a large extent. In both  
25 cases, two NO peaks are observed at about 100 and 420°C, and a broad NO<sub>2</sub> desorption

1 profile is seen from 50 to 450°C. This NO<sub>2</sub> feature exhibits two maxima at low and high  
2 temperatures. The high temperature maximum is close to 350°C and is not affected by the  
3 introduction of Pd. In contrast, the low temperature maximum shifts from 116 to 136°C when  
4 Pd is added to CZ (Fig. 6c). For both samples, the quantities of adsorbed and desorbed NO<sub>x</sub>  
5 closely match (Table 2). Table 2 shows that the amount of adsorbed NO<sub>x</sub> fluctuates to some  
6 extent. This was related to slightly different times of exposure and not to differences in the  
7 starting conditions of the samples. In agreement with previous work [67], PdO/SiO<sub>2</sub> did not  
8 chemisorb NO<sub>x</sub>. Consequently, the TPD in C<sub>3</sub>H<sub>6</sub>-O<sub>2</sub> after NO<sub>x</sub> chemisorption was not  
9 performed.

10

#### 11 *3.1.8. Adsorption of NO-O<sub>2</sub> – TPD in C<sub>3</sub>H<sub>6</sub>-O<sub>2</sub>*

12 After exposure of the samples to a NO-O<sub>2</sub> mixture, the TPD profiles obtained in C<sub>3</sub>H<sub>6</sub>-  
13 O<sub>2</sub> are shown in Fig. 7 for CZ and Pd(0.89)/CZ. Before TPD, the samples were flushed by N<sub>2</sub>  
14 to remove physisorbed NO<sub>x</sub> and then contacted with the desorption gas mixture (C<sub>3</sub>H<sub>6</sub>-O<sub>2</sub>) for  
15 a few minutes at RT. For both samples, a C<sub>3</sub>H<sub>6</sub> desorption profile is observed at low  
16 temperature. It is worth mentioning that in the case of the oxidation of C<sub>3</sub>H<sub>6</sub> by O<sub>2</sub> without  
17 pre-adsorption of NO<sub>x</sub> (not shown), a similar desorption feature was observed. This low  
18 temperature desorption feature is, thus, attributed to propene species chemisorbed on catalytic  
19 sites different from those occupied by adsorbed NO<sub>x</sub> species. For both catalysts, HC  
20 consumption starts at 80°C and a more drastic HC consumption is observed at about 110°C. It  
21 is worthwhile mentioning that the HC consumption profile is slightly different for  
22 Pd(0.89)/CZ compared with that of CZ. At temperatures higher than 150°C, the HC  
23 concentration reaches its input concentration for CZ (Fig. 7a). This phenomenon, however, is  
24 not observed for Pd(0.89)/CZ (Fig. 7b). The first column of Table 3 shows that the light-off

1 temperature of  $C_3H_6$  in the course of the TPD in  $C_3H_6-O_2$  decreases drastically with the  
2 addition of Pd.

3         Considering desorption of the  $N_tO_x$  ( $NO$ ,  $NO_2$  and  $N_2O$ ) species, rather complicated  
4 profiles are observed (Fig. 7). A detailed description of the traces seen for CZ is reported in a  
5 recent article [38]. The amounts of adsorbed and desorbed  $N_tO_x$  species are listed in Table 2.  
6 For both catalysts, a comparison of the desorbed quantities (Table 2) and profiles of  $N_tO_x$   
7 species of the two TPD experiments either in  $N_2$  (Fig. 6) or in  $C_3H_6-O_2$  (Fig. 7) after exposure  
8 of the samples to  $NO-O_2$  shows striking differences. First,  $NO$  becomes the major  $N_tO_x$   
9 species of the TPD in  $C_3H_6-O_2$ . In contrast,  $NO_2$  is the major species of the TPD in  $N_2$ .  
10 Second, the global amount of desorbed  $N_tO_x$  species, taking into account that  $N_2O$  originates  
11 from the recombination of two  $NO_x$  molecules, is always lower than that adsorbed for the  
12 TPD in  $C_3H_6-O_2$ . On the other hand, adsorbed and desorbed  $NO_x$  quantities agree well for the  
13 TPD in  $N_2$ . These results suggest that part of the adsorbed  $NO_x$  is reduced to  $N_2$  in the  
14 presence of  $C_3H_6$  in the desorption mixture. Finally, the  $N_tO_x$  TPD profiles (Fig. 7) suggest  
15 that part of the adsorbed  $NO_x$  species reacted with  $C_3H_6$  in the low temperature region (50-  
16  $115^\circ C$ ). For  $N_tO_x$  species, the  $NO_x$  desorption feature is clearly truncated in this low  
17 temperature region compared to that of the TPD in  $N_2$  (Fig. 6). As already discussed [38],  
18 these concomitant consumptions suggest the interaction of adsorbed  $NO_x$  species ( $ad-NO_x$ )  
19 with propene and the formation of mixed compounds ( $R-NO_x$ ) stored on the catalytic  
20 material. For Pd(0.89)/CZ, it is worth adding that a stabilised HC consumption occurs up to  
21 higher temperatures, ca.  $150^\circ C$ , compared with that observed on CZ (Fig. 7). Overall, the  
22 broad  $N_tO_x$  desorption features observed at low temperatures ( $100-200^\circ C$ ) over CZ become  
23 thinner over Pd(0.89)/CZ, whereas those at high temperatures ( $220-400^\circ C$ ) are clearly shifted  
24 to lower temperatures ( $200-300^\circ C$ ) with the incorporation of Pd. In addition, the amount of

1 NO<sub>2</sub> desorbed at temperatures higher than 200°C is much lower over Pd(0.89)/CZ than over  
2 CZ. That of N<sub>2</sub>O is, however, greater.

3

#### 4 *3.1.9. C<sub>3</sub>H<sub>6</sub> oxidation by O<sub>2</sub>*

5 Fig. 8 shows that the C<sub>3</sub>H<sub>6</sub> oxidation profiles are obviously different depending on the  
6 nature of the catalyst support.

7 On Pd(0.89)/CZ, C<sub>3</sub>H<sub>6</sub> oxidation is rather similar to that observed after adsorption of  
8 NO-O<sub>2</sub> (Fig. 7b) with comparable light-off temperature (Table 3). On such a catalyst,  
9 however, the consumption of C<sub>3</sub>H<sub>6</sub> in the C<sub>3</sub>H<sub>6</sub>-O<sub>2</sub> reaction starts at a higher temperature and  
10 is more pronounced before 250°C than after adsorption of NO-O<sub>2</sub>. In contrast, C<sub>3</sub>H<sub>6</sub> oxidation  
11 proceeds much more steeply in a much narrower range of temperature (from 195 to 260°C) on  
12 Pd(0.93)/SiO<sub>2</sub> than on Pd(0.89)/CZ (Fig. 8). In addition, C<sub>3</sub>H<sub>6</sub> does not chemisorb at RT on  
13 Pd(0.93)/SiO<sub>2</sub>, as is the case of Pd(0.89)/CZ that shows a low temperature C<sub>3</sub>H<sub>6</sub> desorption  
14 feature. For Pd(0.93)/SiO<sub>2</sub>, it is worthwhile noting that the experiment reported on Fig. 8 was  
15 carried out after a previous C<sub>3</sub>H<sub>6</sub>-NO-O<sub>2</sub> Temperature-Programmed Surface Reaction (TPSR).  
16 It will be shown later (please refer to part 3.1.10.) that for Pd(0.93)/SiO<sub>2</sub> such an experimental  
17 sequence does significantly influence the light-off temperature of C<sub>3</sub>H<sub>6</sub>, whereas it has no  
18 impact on CZ-supported catalysts.

19 Table 3 shows that the C<sub>3</sub>H<sub>6</sub> light-off temperature for the C<sub>3</sub>H<sub>6</sub>-O<sub>2</sub> reaction is the  
20 lowest for Pd(0.93)/SiO<sub>2</sub> and the highest for CZ. Finally, Pd promotes significantly C<sub>3</sub>H<sub>6</sub>  
21 oxidation for the CZ-based catalysts.

22

#### 23 *3.1.10. C<sub>3</sub>H<sub>6</sub>-NO-O<sub>2</sub> TPSR experiment*

24 TPSR of the complete reacting mixture was performed after exposure of Pd(0.89)/CZ  
25 to the reacting mixture at RT (Fig. 9). The features observed are comparable to those seen for

1 the TPD in C<sub>3</sub>H<sub>6</sub>-O<sub>2</sub> after adsorption of NO-O<sub>2</sub> (Fig. 7b). NO desorption is the major N<sub>t</sub>O<sub>x</sub>  
2 species with a two peak profile (100 and 220°C). The formation of NO<sub>2</sub> and N<sub>2</sub>O are,  
3 however, more limited than those obtained for the TPD experiment in C<sub>3</sub>H<sub>6</sub>-O<sub>2</sub> (Fig. 7). C<sub>3</sub>H<sub>6</sub>  
4 and NO<sub>x</sub> consumptions detected in the low temperature region in the case of the TPD  
5 experiment in C<sub>3</sub>H<sub>6</sub>-O<sub>2</sub> are no longer observed. C<sub>3</sub>H<sub>6</sub> is moderately consumed from 100 to  
6 200°C and at higher temperatures the oxidation of C<sub>3</sub>H<sub>6</sub> accelerates. More interesting is that  
7 the NO<sub>x</sub> profile shows a decrease of the NO<sub>x</sub> concentration at 297°C corresponding to 50% of  
8 the NO<sub>x</sub> inlet concentration. At this temperature, the conversion of C<sub>3</sub>H<sub>6</sub> is 79%. At higher  
9 temperatures, the NO<sub>x</sub> concentration reaches back its inlet concentration, and NO is oxidized  
10 to NO<sub>2</sub> when full conversion of C<sub>3</sub>H<sub>6</sub> is achieved at about 400°C.

11 Compared with the TPSR profiles found on CZ (Fig. 12 of [38]), the desorption peak  
12 of NO reported in this experiment at about 300°C is no longer observed in the course of the  
13 TPSR on Pd(0.89)/CZ, as a NO<sub>x</sub> deficit occurs in this temperature range (Fig. 9).

14 The TPSR profiles of Pd(0.93)/SiO<sub>2</sub> (not shown) are less complicated than those of  
15 Pd(0.89)/CZ. The most interesting peculiarity is that if the temperature is decreased from  
16 500°C to RT (reverse TPSR) after the first TPSR experiment, the C<sub>3</sub>H<sub>6</sub> light-off temperature  
17 and the selectivity to N<sub>2</sub> are modified significantly. The C<sub>3</sub>H<sub>6</sub> light-off temperature and the N<sub>2</sub>  
18 selectivity of the TPSR and the reverse TPSR decrease from 298 to 237°C (Table 3) and from  
19 70 to 30%, respectively. On the other hand, the conversion of NO<sub>x</sub> to N<sub>2</sub> remains almost  
20 constant and close to 9% at maximum NO<sub>x</sub> conversion.

21 Such phenomena were not observed for the CZ-based catalysts for which the C<sub>3</sub>H<sub>6</sub> and NO<sub>x</sub>  
22 profiles of the TPSR and the reverse TPSR were comparable.

23 As in the case of the C<sub>3</sub>H<sub>6</sub>-O<sub>2</sub> reaction, Table 3 shows that the C<sub>3</sub>H<sub>6</sub> light-off  
24 temperature for the TPSR is lowest for Pd(0.93)/SiO<sub>2</sub> and highest for CZ. Pd also promotes  
25 significantly C<sub>3</sub>H<sub>6</sub> oxidation for the CZ-based catalysts.

### 1 3.1.11. Steady-state NO-C<sub>3</sub>H<sub>6</sub>-O<sub>2</sub> reaction

2 Prior to steady-state measurements, the catalysts were submitted to a TPSR under the  
3 complete reacting mixture from RT to 500°C with a heating rate of 10°C min<sup>-1</sup>.

4 Fig. 10 shows the performances of the catalysts for the reduction of NO<sub>x</sub> under steady-  
5 state conditions with stepwise increase of the temperature. The temperature of maximum of  
6 N<sub>2</sub> formation, the corresponding NO<sub>x</sub> and C<sub>3</sub>H<sub>6</sub> conversions are listed in Table 4.

7 It is obvious that the introduction of Pd leads to a significant increase of NO<sub>x</sub>  
8 reduction to N<sub>2</sub> as well as a drastic decrease of the C<sub>3</sub>H<sub>6</sub> light-off temperature. Table 3 lists  
9 the temperature of light-off of C<sub>3</sub>H<sub>6</sub> over various Pd-containing catalysts with respect to  
10 reaction conditions. From this table it can also be concluded that the presence of NO does not  
11 influence this light-off temperature, as was the case for CZ ([38] and first line of Table 3).

12 Conversion of NO<sub>x</sub> to N<sub>2</sub> higher than 20% is obtained on the Pd/CZ catalysts. On the  
13 other hand, Pd(0.93)/SiO<sub>2</sub> shows a rather low conversion of NO<sub>x</sub> to N<sub>2</sub> close to that found for  
14 CZ, despite the fact that the light-off temperature of propene is similar to that of the most  
15 active CZ-based catalyst (Pd(0.89)/CZ). One also may note that propene oxidation is steeper  
16 over Pd(0.93)/SiO<sub>2</sub> than over Pd/CZ catalysts. It is worthwhile noting that N<sub>2</sub> selectivity is  
17 higher than 80% on CZ-based catalysts, whereas that of Pd(0.93)/SiO<sub>2</sub> is of 28% (Table 4).  
18 Finally, Fig. 10e shows that NO oxidation to NO<sub>2</sub> is almost eliminated in the presence of  
19 C<sub>3</sub>H<sub>6</sub> before 400°C, the temperature of which corresponds to the almost complete conversion  
20 of C<sub>3</sub>H<sub>6</sub> (Fig. 10c).

21 To illustrate the high stability of the CZ-supported catalysts, Table 5 reports on the  
22 influence of time on stream on the reduction of NO<sub>x</sub> on Pd(0.89)/CZ. This catalyst exhibits  
23 NO<sub>x</sub> conversion to N<sub>2</sub> by about 30% and does not deactivate in the absence of water for 1 h.  
24 After about 1 hour of run, 1.7% of water was introduced in the reaction mixture. This addition  
25 decreases the conversion of NO<sub>x</sub> by about 10%. More interesting is that the catalyst does not

1 deactivate over a period of 19 hours on stream in the presence of water. After 19 hours on  
2 stream, the initial activity is restored when water is removed from the feed. This suggests that  
3 H<sub>2</sub>O competes with the active sites responsible for N<sub>2</sub> formation. C<sub>3</sub>H<sub>6</sub> conversion remains  
4 almost unaffected and close to 60%. Chemical analysis of this sample after reaction reveals a  
5 carbon content of only 0.4 wt%.

6

### 7 *3.1.12. Steady-state NO-C<sub>3</sub>H<sub>6</sub>-O<sub>2</sub> reaction over mechanical mixtures*

8 The results obtained over two mechanical mixtures of Pd(0.89)/CZ + SiO<sub>2</sub> and  
9 Pd(0.93)/ SiO<sub>2</sub> + CZ are shown in Fig. 11. It is obvious that the mechanical mixture of  
10 Pd(0.89)/CZ + SiO<sub>2</sub> (Fig. 11a) is more active than its counterpart (Fig. 11b) over a wide range  
11 of temperature. Table 6 compares the performances of the mechanical mixtures at about  
12 250°C. Given that SiO<sub>2</sub> exhibits no deNO<sub>x</sub>, the activity reported for the mechanical mixture of  
13 Pd(0.89)/CZ and SiO<sub>2</sub> is only due to Pd(0.89)/CZ. It is quite unusual to note that the HSV  
14 does not influence the performance of the Pd(0.89)/CZ catalyst as the experiments carried out  
15 with 0.10 or 0.20 g of this sample give comparable deNO<sub>x</sub> activities (Table 4 and Table 6,  
16 Fig. 10d and Fig. 11a). This unexpected result suggests that the geometry of the reactor used  
17 in this study was not the best to achieve optimised deNO<sub>x</sub> conversions. The deNO<sub>x</sub> activity  
18 reported for the mechanical mixture made up of Pd(0.93)/SiO<sub>2</sub> and CZ roughly corresponds to  
19 the sum of the activities of both catalytic systems. These conclusions are corroborated by the  
20 selectivity to N<sub>2</sub> that is: (i) close to that reported for Pd(0.89)/CZ (Table 4) for the mechanical  
21 mixture made up of Pd(0.89)/CZ and SiO<sub>2</sub> (Table 6), and (ii) intermediate to those of  
22 Pd(0.93)/SiO<sub>2</sub> and CZ (Table 4) for the corresponding mechanical mixture (Table 6).

23

24

25

### 1 3.1.13. Steady-state NO-C<sub>3</sub>H<sub>6</sub>OH-O<sub>2</sub> reaction over Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub>

2 Over CZ, C<sub>3</sub>H<sub>6</sub> was substituted by 1-C<sub>3</sub>H<sub>7</sub>OH as reductant. The results of this steady-  
3 state experiment are shown in Fig. 12. In contrast to the steady-state measurements with C<sub>3</sub>H<sub>6</sub>  
4 as reductant (Fig. 10b), CZ exhibits a higher lean deNO<sub>x</sub> activity in the presence of  
5 1-C<sub>3</sub>H<sub>7</sub>OH over a broader range of temperatures than with C<sub>3</sub>H<sub>6</sub>. In comparison, the highest  
6 activity, 19% NO<sub>x</sub> to N<sub>2</sub> at 283°C when 1-C<sub>3</sub>H<sub>7</sub>OH is used as reductant, is more than twice  
7 that listed at 361°C with C<sub>3</sub>H<sub>6</sub> (Table 4). The selectivity to N<sub>2</sub> in the presence of C<sub>3</sub>H<sub>7</sub>OH  
8 (76%) is comparable to that found in the presence of C<sub>3</sub>H<sub>6</sub> (81%).

9

## 10 4. Discussion

11

### 12 4.1. State of Pd in the supported Pd catalysts

13 The XRD pattern of the calcined Pd(0.93)/SiO<sub>2</sub> sample (Fig. 2) indicates, as expected,  
14 the presence of PdO. The corresponding reduced sample exhibits propene hydrogenation  
15 activity (Table 1).

16 As mentioned in the results (part 3.1.3.), due to the overlapping of the diffraction  
17 peaks of PdO with those of CZ, XRD characterisation could not be successfully used to  
18 investigate the nature of the Pd species of the Pd/CZ catalysts. XANES measurements of  
19 oxidised and reduced Pd(0.54)/CZ samples show that they closely resemble those of PdO and  
20 the Pd foil, respectively (Fig. 3). As in the case of Pd/SiO<sub>2</sub>, these XANES measurements  
21 suggest that Pd is present as PdO for the calcined sample (Fig. 3a). Pd/CZ catalysts also  
22 catalyse propene hydrogenation (Table 1), which agrees fairly well with the XANES  
23 measurements of the reduced Pd(0.54)/CZ sample (Fig. 3), indicating the presence of reduced  
24 Pd clusters. Holles and Davis have reported, however, that Pd(4.0)/CeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> could not be  
25 fully reduced even after exposure to CO at 400°C [68]. Comparable conclusions were also

1 drawn by Matsumara and coworkers for Pd(3.0)/CeO<sub>2</sub> and Pd(2.0)/ZrO<sub>2</sub> samples reduced  
2 under H<sub>2</sub> at 300 and 400°C [69,70], respectively. As X-ray absorption spectroscopy is known  
3 to provide an average picture of the targeted metal species [71], CO-FTIR measurements were  
4 also performed on Pd(0.89)/CZ (Fig. 4b). In agreement with XANES measurements, CO-  
5 FTIR spectra recorded after H<sub>2</sub> reduction at 500°C do not reveal the presence of Pd oxidised  
6 species, as is the case with a CZ-supported Rh catalyst [58].

7         The characterisation of these catalysts after oxidising or reducing pretreatments were  
8 motivated due to the initial calcination of the samples and the C<sub>3</sub>H<sub>6</sub>-NO-O<sub>2</sub> TPSR experiment  
9 that was carried out before steady-state measurements, the TPSR experiment leading to the  
10 exposure of the calcined sample to the C<sub>3</sub>H<sub>6</sub> reductant. The characterisation of the Pd/CZ  
11 catalysts indicates that Pd is present as PdO in the calcined samples. Nevertheless, one might  
12 wonder about the nature of the Pd species in the course of the lean NO<sub>x</sub> reaction. Fernàndez-  
13 Garcia et al. have recently shown that even under a stoichiometric C<sub>3</sub>H<sub>6</sub>+CO+NO+O<sub>2</sub>  
14 mixture, Pd was not reduced to Pd<sup>0</sup> for Pd(1.0)/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> up to reaction temperature as high  
15 as 400°C, but remained in an oxidised state due to contact between PdO clusters and ceria-  
16 zirconia [72]. It is, thus, very likely that the same conclusion also applies to the Pd/CZ  
17 catalysts of the present work. This assumption is supported by: (i) the TPR traces revealing  
18 greater interaction of the Pd species with CZ than with SiO<sub>2</sub> (Fig. 1), and (ii) the steady-state  
19 catalytic results (Table 4 and Table 6) that show markedly different N<sub>2</sub> selectivity for Pd/CZ  
20 and Pd/SiO<sub>2</sub> catalysts. The N<sub>2</sub> selectivity found over the Pd/CZ catalysts is, indeed, more than  
21 twice that observed over Pd/SiO<sub>2</sub>. The N<sub>2</sub> selectivity listed for Pd/SiO<sub>2</sub> agrees well with those  
22 already reported over a comparable catalytic system [19], over Pd/Al<sub>2</sub>O<sub>3</sub> [34] or over Pt<sup>0</sup>  
23 clusters [19]. This means that PdO is reduced to Pd<sup>0</sup> when being supported on SiO<sub>2</sub> even  
24 under a lean atmosphere. Such a conclusion has also been reported by Fernàndez-Garcia et al.  
25 for alumina-supported Pd catalysts [72]. As already mentioned above, however, these authors

1 have demonstrated that this was not the case for a Pd(1.0)/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> catalyst. The obvious  
2 higher N<sub>2</sub> selectivity for the Pd/CZ catalysts might also suggest that the deNO<sub>x</sub> mechanism  
3 occurring over these materials is different from the dissociation mechanism reported over  
4 zero-valent PGMs atoms [6,9] and, thus, that the nature of the Pd species of the Pd/CZ  
5 catalysts is different from that of Pd<sup>0</sup>. These arguments are further supported by the  
6 comparison of the light-off of C<sub>3</sub>H<sub>6</sub> of the TPSR and reverse TPSR (see part 3.1.10.) that  
7 decreases to a significant extent on Pd(0.93)/SiO<sub>2</sub>, and it is hardly affected at all on Pd/CZ  
8 catalysts. Under the experimental conditions of the present study, it is, therefore, very likely  
9 that Pd is present as PdO<sub>x</sub> species, with x close to unity [73], rather than Pd<sup>0</sup>.

10

#### 11 *4.2. Lean deNO<sub>x</sub> mechanism proposal over PdO<sub>x</sub>/CZ catalysts*

12 The results of the present work show that the incorporation of Pd to CZ promotes  
13 significantly lean deNO<sub>x</sub> activity (Fig. 10). In addition, CZ-supported catalysts exhibit a much  
14 higher N<sub>2</sub> selectivity compared with that of Pd<sup>0</sup>(0.93)/SiO<sub>2</sub> (Table 4). Centi et al. [31] and  
15 Liotta et al. [32] have also recently reported elevated N<sub>2</sub> selectivities over Pt/Ce<sub>0.60</sub>Zr<sub>0.40</sub>O<sub>2</sub>-  
16 Al<sub>2</sub>O<sub>3</sub> and Pt/Ce<sub>0.60</sub>Zr<sub>0.40</sub>O<sub>2</sub> catalysts. These authors, however, did not comment about this  
17 peculiarity. As already mentioned in the preceding characterisation section, this obvious  
18 difference in N<sub>2</sub> selectivity between Pd<sup>0</sup>/SiO<sub>2</sub> and PdO<sub>x</sub>/CZ catalysts suggests that the lean  
19 deNO<sub>x</sub> mechanism occurring over PdO<sub>x</sub>/CZ catalysts is different from that occurring over  
20 Pd<sup>0</sup>/SiO<sub>2</sub>. The fairly low N<sub>2</sub> selectivity found for Pd<sup>0</sup>/SiO<sub>2</sub> (Table 4) indicates that lean deNO<sub>x</sub>  
21 most likely proceeds through the NO dissociation mechanism [9] on zero-valent Pd clusters,  
22 the oxygen left from NO dissociation on the reduced surface being "cleaned" by the C<sub>3</sub>H<sub>6</sub>  
23 oxidation reaction.

24 In a recent article [38], we suggested that reaction intermediates such as NO<sub>2</sub>, organic  
25 nitrogen-containing compounds (RNO<sub>x</sub>) and oxygenates (C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>) might be involved in the

1 lean deNO<sub>x</sub> catalysis on CZ. In the proposed mechanism, the production of NO<sub>2</sub> and C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>,  
2 the formation of the latter resulting from the decomposition of R-NO<sub>x</sub> intermediates produced  
3 by the reaction of NO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>, has been assumed to be critical for lean deNO<sub>x</sub> activity, as  
4 also reported by other authors [34]. The present study also shows that NO oxidation to NO<sub>2</sub> is  
5 achieved on the bare support, as the introduction of Pd does not promote such a reaction (Fig.  
6 5). This conclusion is consistent with the work of Krishna et al. in which the authors reported  
7 that CeO<sub>2</sub> is a fairly efficient catalyst in the oxidation of NO [74].

8         The activation of C<sub>3</sub>H<sub>6</sub> proceeds unambiguously on the PdO<sub>x</sub> catalytic function, as  
9 demonstrated by the C<sub>3</sub>H<sub>6</sub> light-off temperature that decreases significantly over supported Pd  
10 catalysts (Fig. 10 and Table 3). In addition, it is obvious that this low temperature activation  
11 of C<sub>3</sub>H<sub>6</sub> is responsible for the lean deNO<sub>x</sub> activity of PdO<sub>x</sub>/CZ catalysts, as both C<sub>3</sub>H<sub>6</sub>  
12 activation and deNO<sub>x</sub> occur concomitantly (Fig. 9 and Fig. 10c,d).

13         One might, however, wonder about the activation process of C<sub>3</sub>H<sub>6</sub> in the course of the  
14 deNO<sub>x</sub> reaction. On that point, the TPD in C<sub>3</sub>H<sub>6</sub>-O<sub>2</sub> after adsorption of NO-O<sub>2</sub> is very  
15 informative. Fig. 7b shows that C<sub>3</sub>H<sub>6</sub> is activated through ad-NO<sub>2</sub> species, as already  
16 proposed on CZ [38], the low temperature (130-180°C) consumption of C<sub>3</sub>H<sub>6</sub> being different  
17 from the C<sub>3</sub>H<sub>6</sub> profiles observed in the C<sub>3</sub>H<sub>6</sub>-O<sub>2</sub> reaction on Pd(0.89)/CZ (Fig. 8) and in the  
18 TPD in C<sub>3</sub>H<sub>6</sub>-O<sub>2</sub> after adsorption of NO-O<sub>2</sub> on CZ (Fig. 7a). In this temperature range, it is  
19 worthwhile noting that the NO<sub>2</sub> concentration of the TPD in N<sub>2</sub> after adsorption of NO-O<sub>2</sub> on  
20 Pd(0.89)/CZ is greater than that of CZ (Fig. 6c, 130-180°C region). These observations  
21 strongly suggest that NO<sub>2</sub> species adsorbed on the PdO<sub>x</sub> catalytic function account for the  
22 activation of C<sub>3</sub>H<sub>6</sub>. Such a conclusion is also supported by the fact that NO is mainly  
23 desorbed in the TPD in C<sub>3</sub>H<sub>6</sub>-O<sub>2</sub> after adsorption of NO-O<sub>2</sub> (Table 2), whereas NO<sub>2</sub> would  
24 have been expected to be the most abundant desorbed compound from the TPD in N<sub>2</sub> (Table 2  
25 and Fig. 6b). As discussed previously [38], the activation of C<sub>3</sub>H<sub>6</sub> by ad-NO<sub>2</sub> and the

1 concomitant release of NO might be attributed to the intermediate formation of R-NO<sub>x</sub>  
2 compounds, the decomposition of which produces NO and C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>.

3         One might wonder whether lean deNO<sub>x</sub> also occurs on the PdO<sub>x</sub> catalytic function.  
4 Given that lean deNO<sub>x</sub> occurs to a significant extent on CZ when C<sub>3</sub>H<sub>6</sub> is substituted by 1-  
5 C<sub>3</sub>H<sub>7</sub>OH (Fig. 12), it seems more likely that NO reduction takes place via a lacunar  
6 mechanism on reduced CZ sites, as proposed by several groups [75-78]. These authors,  
7 indeed, provided evidence for the decomposition of NO to N<sub>2</sub> on prereduced CeO<sub>2</sub> surfaces. It  
8 is worth reporting that this decomposition pathway has also been considered in Three-Way  
9 Catalysis in which CO is used as reductant [15]. In the course of the lean deNO<sub>x</sub> reaction, the  
10 creation of the sites responsible for the decomposition of NO would, thus, be achieved by  
11 reduction of CZ by the oxygenates (C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>) produced by the decomposition of R-NO<sub>x</sub>  
12 formed on the PdO<sub>x</sub> catalytic function.

13         The corresponding detailed mechanism of the C<sub>3</sub>H<sub>6</sub>-assisted decomposition of NO on  
14 PdO<sub>x</sub>/CZ catalysts is described in Fig. 13. This mechanism stresses the key role of NO<sub>2</sub>, R-  
15 NO<sub>x</sub> and C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> as intermediates of the Selective Catalytic Reduction (SCR) of NO<sub>x</sub> by  
16 hydrocarbons, as also suggested in many studies [34,38 and references therein]. The proposed  
17 mechanism is consistent with previous studies of Djega-Mariadassou [16,79] who reported  
18 that three catalytic functions were required for the occurrence of the SCR of NO<sub>x</sub> by  
19 hydrocarbons. In this model, CZ achieves both NO oxidation to NO<sub>2</sub> (cycle 1) and NO  
20 decomposition to N<sub>2</sub> (cycle 3), whereas PdO<sub>x</sub> activates C<sub>3</sub>H<sub>6</sub> via ad-NO<sub>2</sub> species (cycle 2)  
21 intermediately producing R-NO<sub>x</sub> compounds that further decompose to NO and C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>. The  
22 role of the latter oxygenates is to reduce CZ to provide the catalytic sites responsible for NO  
23 decomposition (catalytic cycle 3). In the proposed mechanism, the reaction of NO<sub>2</sub> with C<sub>3</sub>H<sub>6</sub>  
24 to give NO back and the competition between the NO oxidation and decomposition reactions  
25 on the CZ catalytic sites also account for the limited formation of NO<sub>2</sub> in the course of the

1 lean deNO<sub>x</sub> process (Fig. 7b, Fig. 9 and Fig. 10e). At elevated temperatures, complete  
2 oxidation of C<sub>3</sub>H<sub>6</sub> by molecular O<sub>2</sub> becomes predominant [80] on PdO<sub>x</sub>, and the deNO<sub>x</sub>  
3 process cannot proceed further.

4

## 5 **5. Conclusion**

6 This study shows that the incorporation of Pd to CZ greatly promotes the reduction of  
7 NO in the presence of C<sub>3</sub>H<sub>6</sub>. These catalysts display very stable deNO<sub>x</sub> activity even in the  
8 presence of 1.7% water, the addition of which induces a reversible deactivation of about 10%.

9 Ex situ characterisation of the catalysts through propene hydrogenation reaction, XRD,  
10 XANES, CO absorption followed by FTIR along with the catalytic results indicate that PdO is  
11 reduced to Pd<sup>0</sup> clusters on Pd/SiO<sub>2</sub>, this catalyst having been studied as a reference catalyst.  
12 This complete reduction process, however, does not occur for PdO<sub>x</sub>/CZ catalysts under our  
13 experimental conditions.

14 The PdO<sub>x</sub>/CZ catalysts also exhibit much higher selectivity to N<sub>2</sub> than that of  
15 Pd<sup>0</sup>/SiO<sub>2</sub>, the selectivity of which is consistent with those already reported in literature data  
16 over supported zero-valent noble metal catalysts. The much higher N<sub>2</sub> selectivity obtained on  
17 PdO<sub>x</sub>/CZ suggests that the lean deNO<sub>x</sub> mechanism occurring on these catalysts is different  
18 from that occurring on Pd<sup>0</sup>/SiO<sub>2</sub> which consists of the dissociation of NO on reduced  
19 palladium sites, followed by the regeneration of the active Pd<sup>0</sup> sites by C<sub>3</sub>H<sub>6</sub>. The results of  
20 the catalytic experiments led us to propose a detailed mechanism (Fig. 13) for which CZ  
21 achieves both NO oxidation to NO<sub>2</sub> and NO decomposition to N<sub>2</sub>, whereas PdO<sub>x</sub> activates  
22 C<sub>3</sub>H<sub>6</sub> via ad-NO<sub>2</sub> species, intermediately producing R-NO<sub>x</sub> compounds that further  
23 decompose to NO and C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>. The role of the latter oxygenates is to reduce CZ to provide  
24 the catalytic sites responsible for NO decomposition. Finally, the proposed C<sub>3</sub>H<sub>6</sub>-assisted NO

1 decomposition mechanism stresses the key role of NO<sub>2</sub>, R-NO<sub>x</sub> and C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> as intermediates  
2 of the Selective Catalytic Reduction (SCR) of NO<sub>x</sub> by hydrocarbons.

3

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9

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**Table 1:** Determination of the percentage of exposed zero-valent Pd atoms ( $\text{Pd}^0$ ) over  $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$  (CZ)- and silica-supported catalysts by means of propene hydrogenation reactions [48].

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Catalysts	Pd(0.54)/CZ	Pd(0.89)/CZ	Pd(0.93)/SiO <sub>2</sub>
$\text{Pd}^0$ (%)	17	16	22

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**Table 2:** Amounts of adsorbed or desorbed NO<sub>x</sub> (NO+ NO<sub>2</sub>) and desorbed N<sub>2</sub>O in the course of the TPD experiments after exposure of the catalysts to NO-O<sub>2</sub> (340 ppm – 8%) in N<sub>2</sub>

Catalysts	experiment	Amounts of adsorbed (ads.) or desorbed (des.) species (10 <sup>-5</sup> mol g <sup>-1</sup> )					
		NO <sub>x ads.</sub>	NO <sub>des.</sub>	NO <sub>2 des.</sub>	NO <sub>x des.</sub>	N <sub>2</sub> O <sub>des.</sub>	N balance*
Ce <sub>0.68</sub> Zr <sub>0.32</sub> O <sub>2</sub> (CZ)	TPD in N <sub>2</sub>	54.8	8.1	46.5	54.6	0.0	0.1
	TPD in C <sub>3</sub> H <sub>6</sub> -O <sub>2</sub>	48.2	19.0	7.8	26.8	5.8	4.9
Pd(0.89)/CZ	TPD in N <sub>2</sub>	47.6	6.2	36.4	42.7	0.0	2.5
	TPD in C <sub>3</sub> H <sub>6</sub> -O <sub>2</sub>	51.8	20.3	5.1	25.4	5.4	7.8

\* N balance calculated with respect to N<sub>2</sub> equivalent

**Table 3:** C<sub>3</sub>H<sub>6</sub> light-off temperatures (°C) of Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> (CZ)- and silica-supported catalysts; 340ppm NO, 8% O<sub>2</sub>, 1900 ppm C<sub>3</sub>H<sub>6</sub> and N<sub>2</sub> balance

	Ads NO-O <sub>2</sub>	Transient	Transient	Steady-state
	TPD in O <sub>2</sub> -C <sub>3</sub> H <sub>6</sub>	O <sub>2</sub> -C <sub>3</sub> H <sub>6</sub>	NO-O <sub>2</sub> -C <sub>3</sub> H <sub>6</sub>	NO-O <sub>2</sub> -C <sub>3</sub> H <sub>6</sub>
CZ	450	473	387	380
Pd(0.54)/CZ	-	277	276	303
Pd(0.89)/CZ	276	251	252	243
Pd(0.93)/SiO <sub>2</sub>	-	-	298*	-
		236	237	237

\* Light-off temperature measured in the course of the first NO-O<sub>2</sub>-C<sub>3</sub>H<sub>6</sub> TPSR

**Table 4:** Temperature of maximum of N<sub>2</sub> formation and percentage of NO<sub>x</sub> converted to N<sub>2</sub> at this temperature over Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> (CZ)-and silica-supported catalysts for the steady-state NO-O<sub>2</sub>-C<sub>3</sub>H<sub>6</sub> reaction (340 ppm - 8 % -1900 ppm, N<sub>2</sub> balance)

Catalysts	CZ	Pd(0.54)/CZ	Pd(0.89)/CZ	Pd(0.93)/SiO <sub>2</sub>
Sample Weight (g)	0.20	0.20	0.20	0.07
T max N <sub>2</sub> (°C)	361	263	243	243
Conversion of NO <sub>x</sub> to N <sub>2</sub> (%)	8	21	29	7
Selectivity to N <sub>2</sub> (%)*	81	83	87	28
C <sub>3</sub> H <sub>6</sub> conversion (%)	34	38	50	58

\* Selectivity to N<sub>2</sub> referred to as  $(N_2/(N_2 + N_2O) \times 100)$

**Table 5:** Influence of the addition of 1.7% water on the conversions of C<sub>3</sub>H<sub>6</sub> and NO<sub>x</sub> to N<sub>2</sub> at 278°C in the course of the C<sub>3</sub>H<sub>6</sub>-NO-O<sub>2</sub> reaction (1900 ppm- 340 ppm – 8 %, balance N<sub>2</sub>) versus time on stream on Pd(0.89)/Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub>.

	Time on stream (h)			
	0	1	20	20.5
H <sub>2</sub> O (%)	0	1.7	1.7	0
Conversion of NO <sub>x</sub> to N <sub>2</sub> (%)	27	24	25	29
Selectivity to N <sub>2</sub> (%)*	75	76	76	77
C <sub>3</sub> H <sub>6</sub> conversion (%)	65	62	62	60

\* Selectivity to N<sub>2</sub> referred to as (N<sub>2</sub>/(N<sub>2</sub> + N<sub>2</sub>O) x 100)

**Table 6:** Percentage of NO<sub>x</sub> converted to N<sub>2</sub> over Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> (CZ)-and silica-supported catalysts for the steady-state NO-O<sub>2</sub>-C<sub>3</sub>H<sub>6</sub> reaction (340 ppm- 8 % -1900 ppm, N<sub>2</sub> balance)

Catalysts	Pd(0.89)/CZ + SiO <sub>2</sub>	Pd(0.93)/SiO <sub>2</sub> + CZ
Sample Weight (g)	0.10 + 0.10	0.10 + 0.10
T (°C)	250	255
Conversion of NO <sub>x</sub> to N <sub>2</sub> (%)	29	12
Selectivity to N <sub>2</sub> (%)*	86	51
C <sub>3</sub> H <sub>6</sub> conversion (%)	47	50

\* Selectivity to N<sub>2</sub> referred to as  $(N_2/(N_2 + N_2O) \times 100)$

## Figure captions

**Fig. 1:** Temperature-Programmed Reduction profiles of the calcined (air 500°C, 2h) catalysts.

**Fig. 2:** XRD patterns of SiO<sub>2</sub>, Pd(0.93)/SiO<sub>2</sub> and Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub>.

**Fig. 3:** XANES spectra at the Pd K edge for PdO (▲), the Pd foil (Δ) and Pd(0.54)/CZ (oxidized in air at 500°C: ---- or reduced in H<sub>2</sub> at 500°C: —).

**Fig. 4:** FT infrared spectra of (a) Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> (CZ) and (b) Pd(0.89)/CZ, reduced under flowing H<sub>2</sub> at 500°C for 2h and evacuation at 500°C for 1h, after introduction of equilibrated pressures of 0.9 (---) and 18 (—) torr of CO.

**Fig. 5:** Steady-state catalytic conversion of NO oxidation to NO<sub>2</sub> in the course of the NO-O<sub>2</sub> reaction (340 ppm - 8%, balance N<sub>2</sub>): (◆) Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> (CZ), (●) Pd(0.54)/CZ.

**Fig. 6:** NO<sub>x</sub> Temperature-Programmed Desorption profiles in N<sub>2</sub> after exposure of the catalysts to NO-O<sub>2</sub> (340 ppm - 8%, balance N<sub>2</sub>) at RT: (a) Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> (CZ), (b) Pd(0.89)/CZ and (c) their comparison, the NO<sub>x</sub> TPD of Pd(0.89)/CZ having been normalised with respect to the amount of NO<sub>x</sub> adsorbed on CZ (Table 2).

**Fig. 7:** Temperature-Programmed Desorption profiles in  $C_3H_6-O_2$  (1900 ppm – 8%  $O_2$ , balance  $N_2$ ) after exposure of the catalysts to  $NO-O_2$  (340 ppm - 8%, balance  $N_2$ ), at RT: (a)  $Ce_{0.68}Zr_{0.32}O_2$  (CZ), (b)  $Pd(0.89)/CZ$ .

**Fig. 8:** Transient  $C_3H_6-O_2$  (1900 ppm - 8%  $O_2$ , balance  $N_2$ ) reaction over  $Pd(0.93)/SiO_2$  and  $Pd(0.89)/Ce_{0.68}Zr_{0.32}O_2$ .

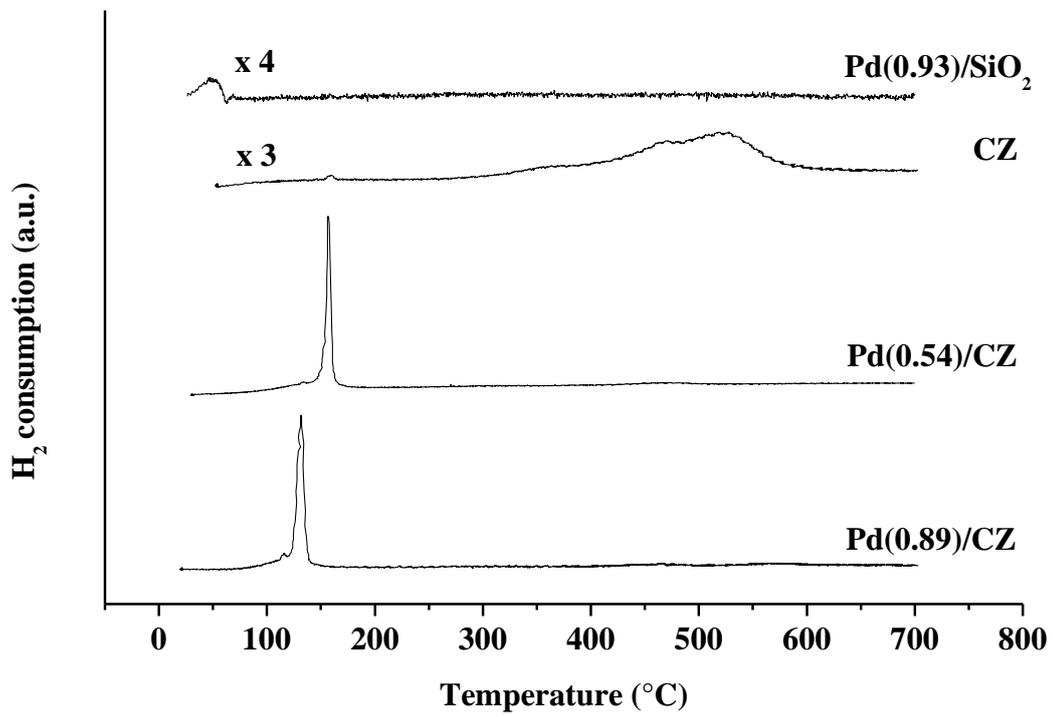
**Fig. 9:** Temperature-Programmed Surface Reaction profiles of  $C_3H_6-NO-O_2$  (1900 ppm - 340 ppm-8%) after exposure of  $Pd(0.89)/Ce_{0.68}Zr_{0.32}O_2$  to  $C_3H_6-NO-O_2$  (1900 ppm - 340 ppm - 8%, balance  $N_2$ ) at RT.

**Fig. 10:** Steady-state catalytic conversions of  $C_3H_6$  and  $NO_x$  to  $N_2$  in the course of the  $C_3H_6-NO-O_2$  reaction (1900 ppm- 340 ppm - 8%, balance  $N_2$ ): (a)  $Pd(0.93)/SiO_2$  (0.07g), (b)  $Ce_{0.68}Zr_{0.32}O_2$  (CZ, 0.20g), (c)  $Pd(0.54)/CZ$  (0.20g), (d)  $Pd(0.89)/CZ$  (0.20g), and of  $NO$  to  $NO_2$  over  $Pd(0.54)/CZ$  (0.20g) (e): (●)  $NO-O_2$  reaction (340 ppm - 8%, balance  $N_2$ ), (○)  $C_3H_6-NO-O_2$  reaction (1900 ppm- 340 ppm - 8%, balance  $N_2$ ).

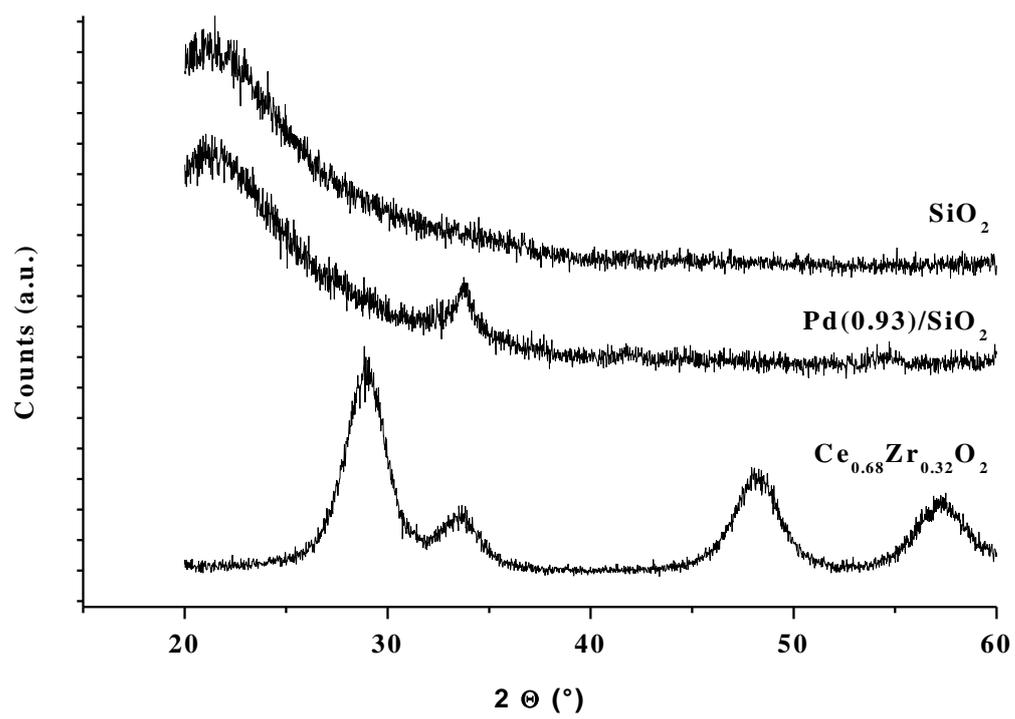
**Fig. 11:** Steady-state catalytic conversions of  $C_3H_6$  and  $NO_x$  to  $N_2$  in the course of the  $C_3H_6-NO-O_2$  reaction (1900 ppm- 340 ppm - 8%, balance  $N_2$ ) of mechanical mixtures: (a)  $Pd(0.89)/Ce_{0.68}Zr_{0.32}O_2 + SiO_2$  (0.10g + 0.10g), (b)  $Pd(0.93)/ SiO_2 + Ce_{0.68}Zr_{0.32}O_2$  (0.10g + 0.10g)

**Fig. 12:** Steady-state catalytic conversions of  $C_3H_7OH$  and  $NO_x$  to  $N_2$  in the course of the  $C_3H_7OH-NO-O_2$  reaction (2200 ppm- 340 ppm - 8%, balance  $N_2$ ) over  $Ce_{0.68}Zr_{0.32}O_2$  (CZ).

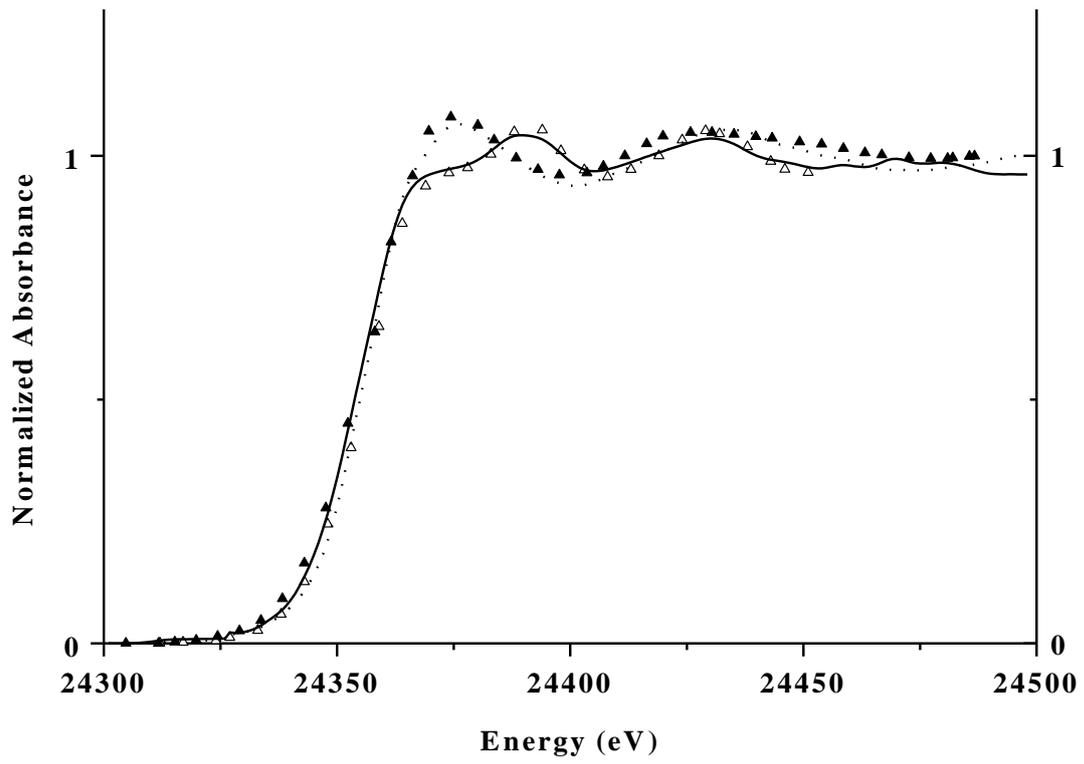
**Fig. 13:** (a) Schematic representation of the catalytic functions, (b) Mechanism of the lean  $C_3H_6$ -assisted decomposition of  $NO$  over  $Pd/Ce_{0.68}Zr_{0.32}O_2$  (CZ) catalysts,  $\boxed{O}$ ,  $R-NO_x$ ,  $C_xH_yO_z$  representing an oxygen from the surface of the CZ support, organic nitrogen-containing and oxygenates compounds of undefined composition, respectively.



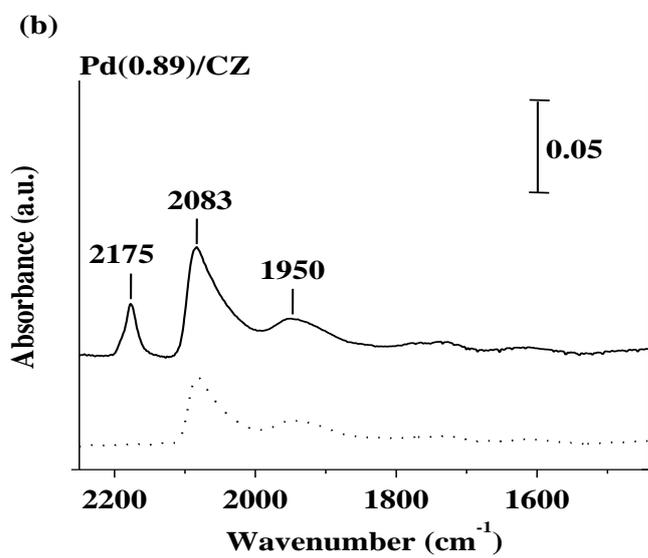
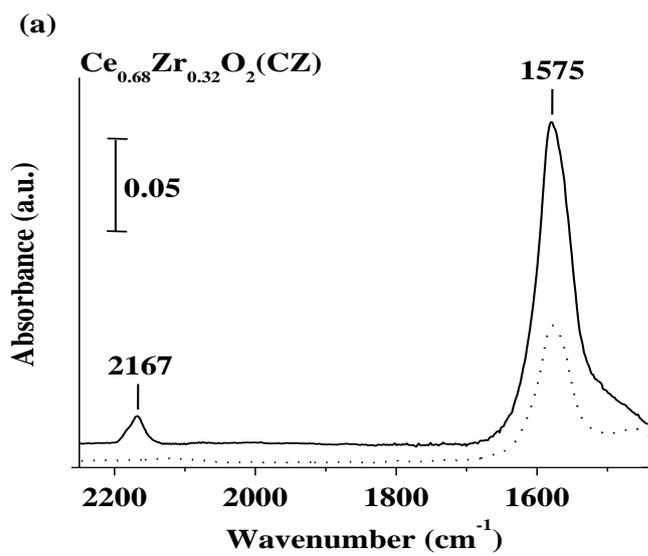
**Fig. 1**



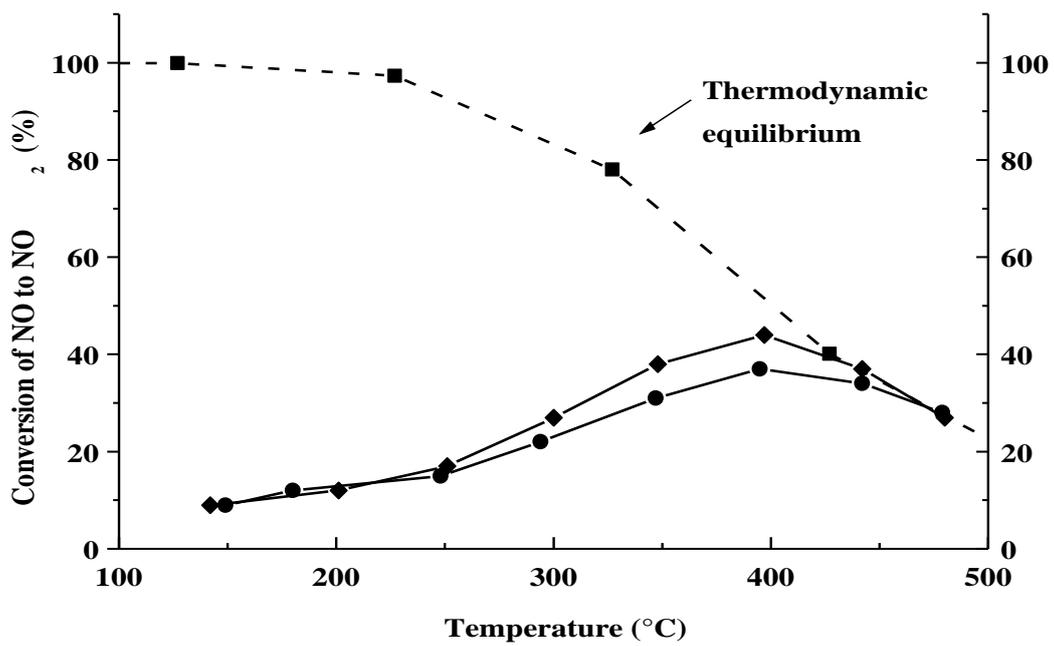
**Fig. 2**



**Fig. 3**



**Fig. 4**



**Fig. 5**

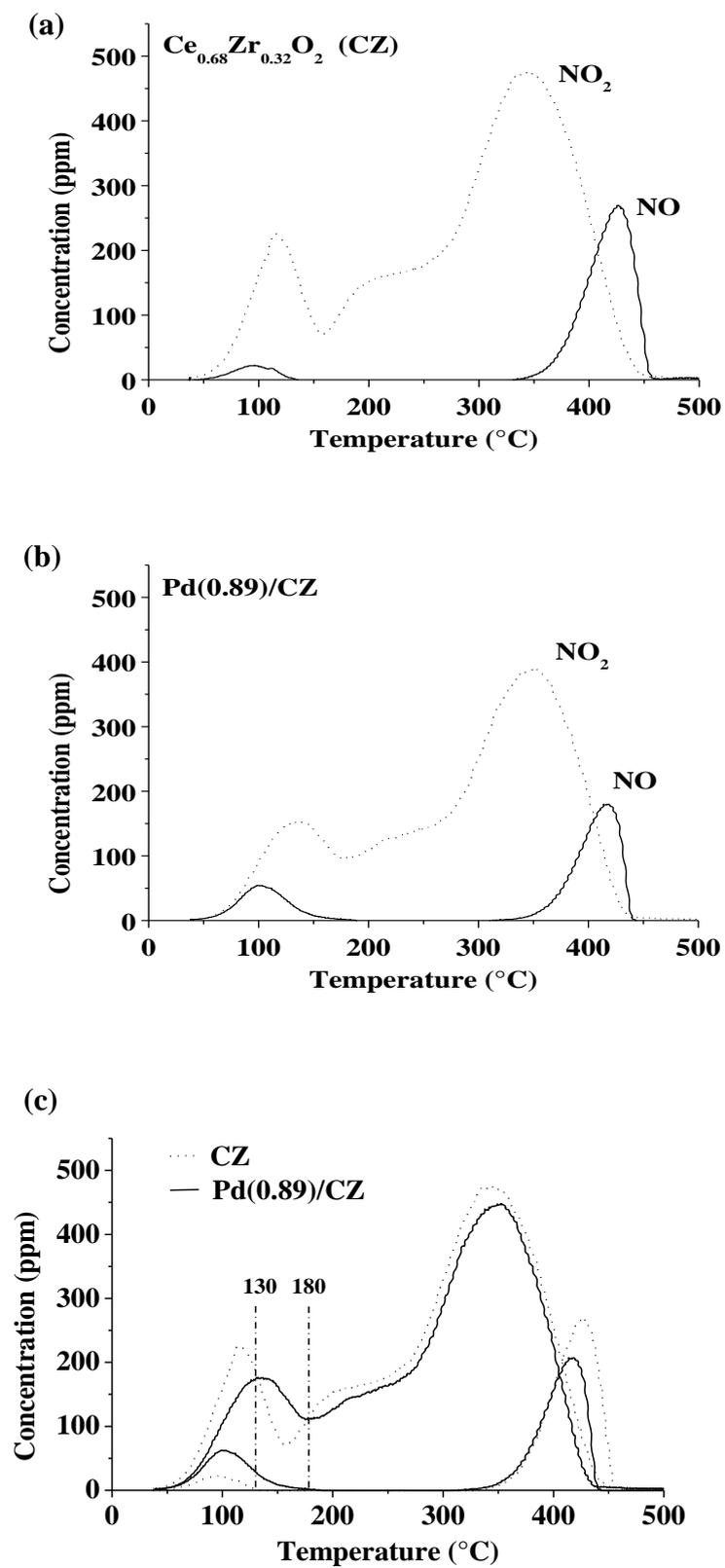
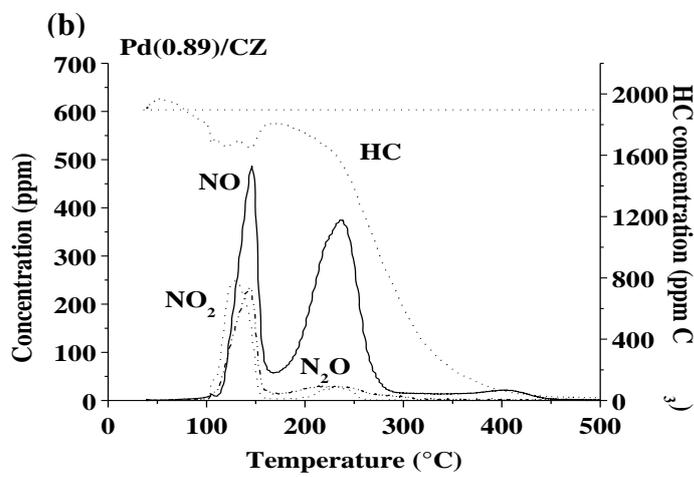
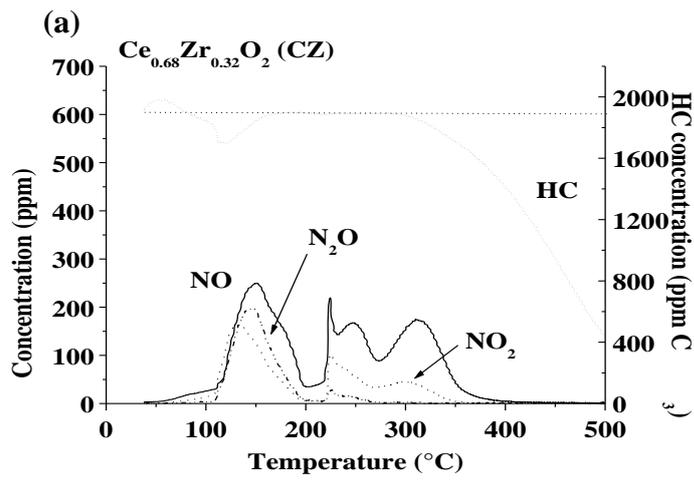
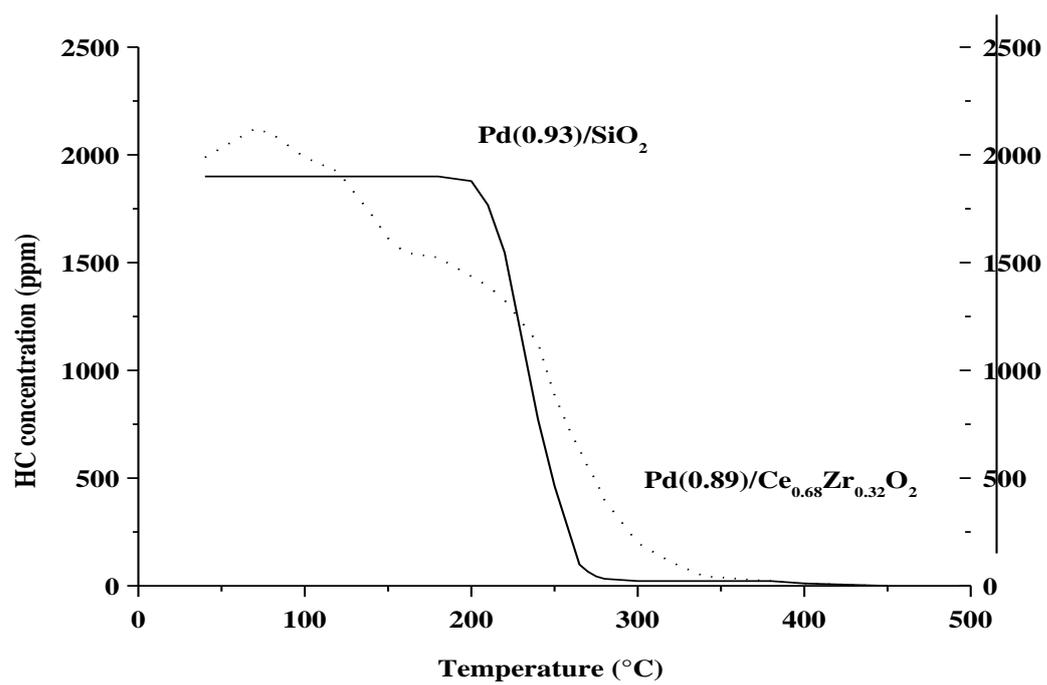


Fig. 6



**Fig. 7**



**Fig. 8**

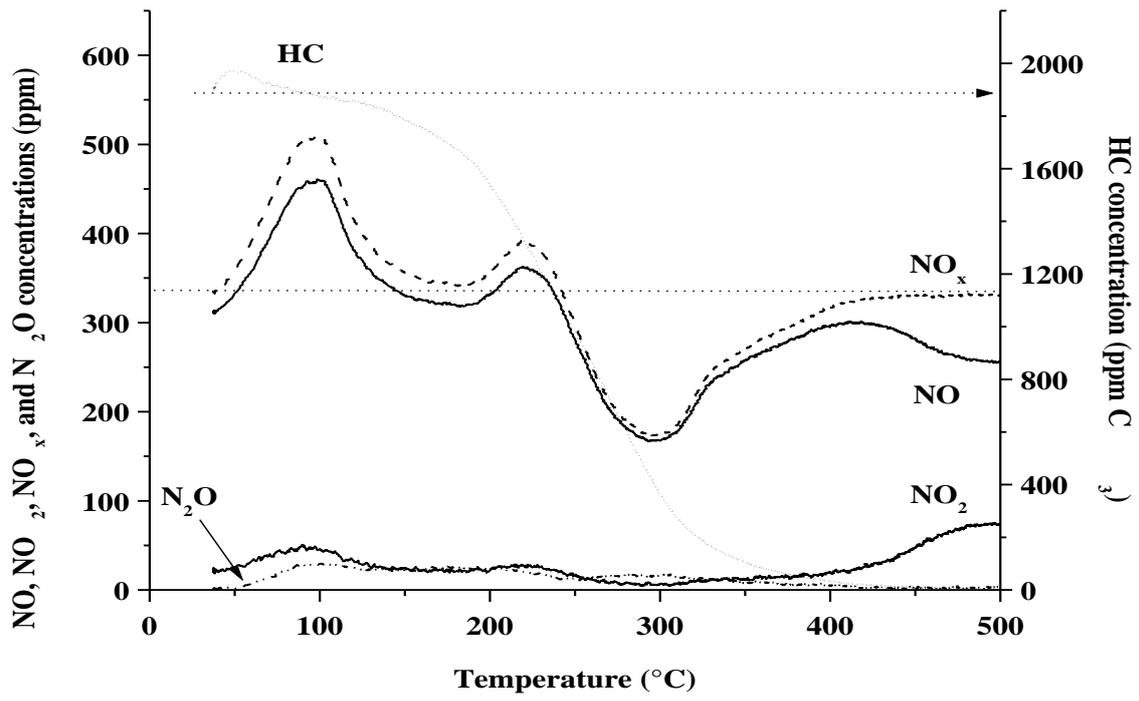


Fig. 9

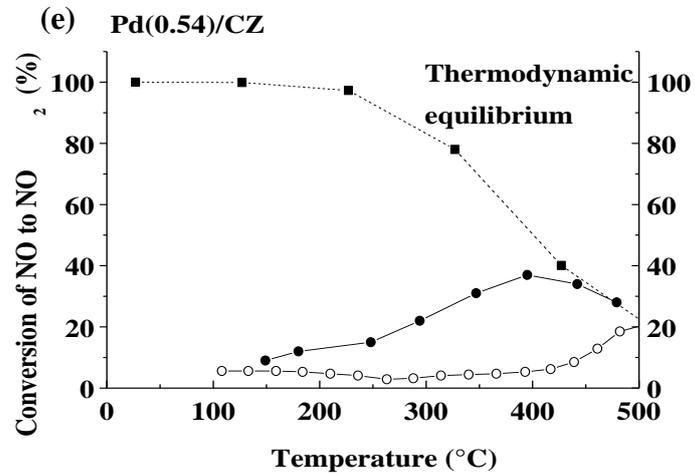
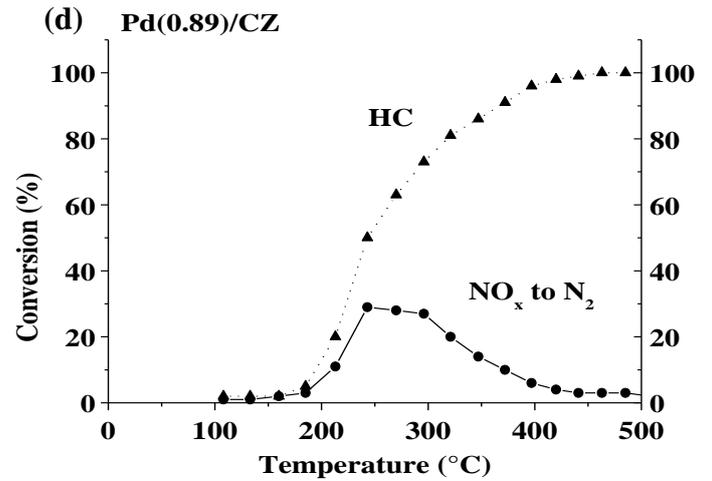
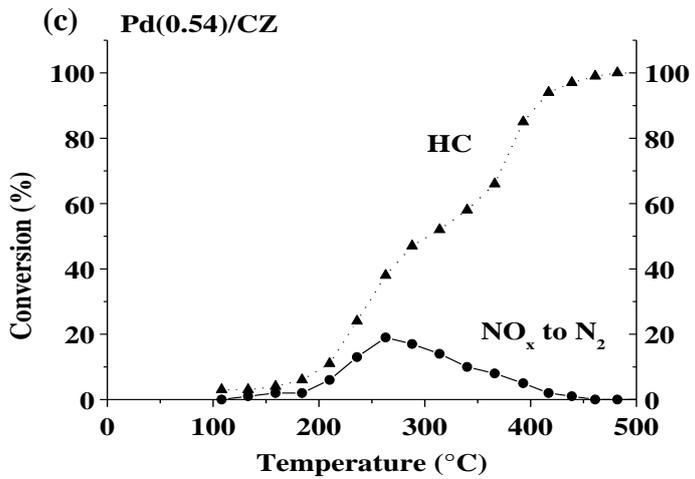
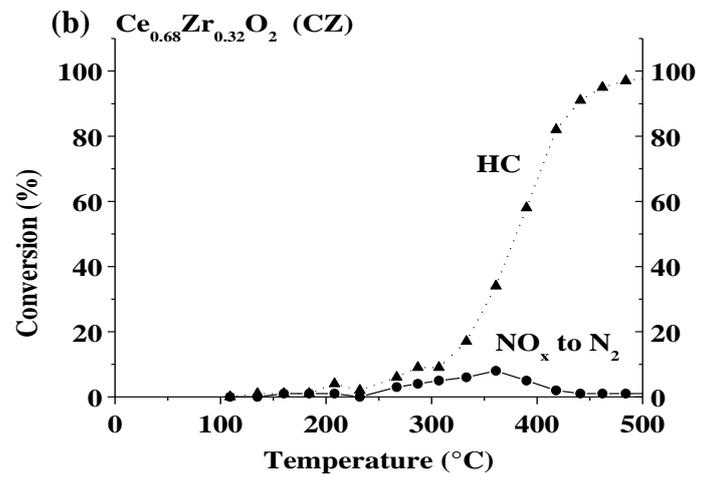
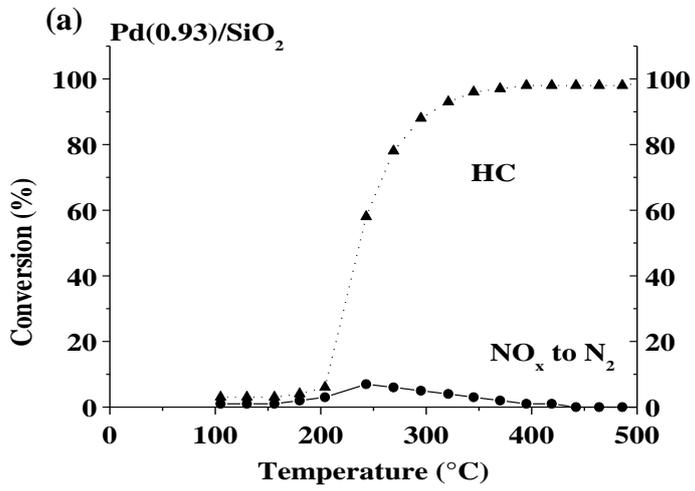
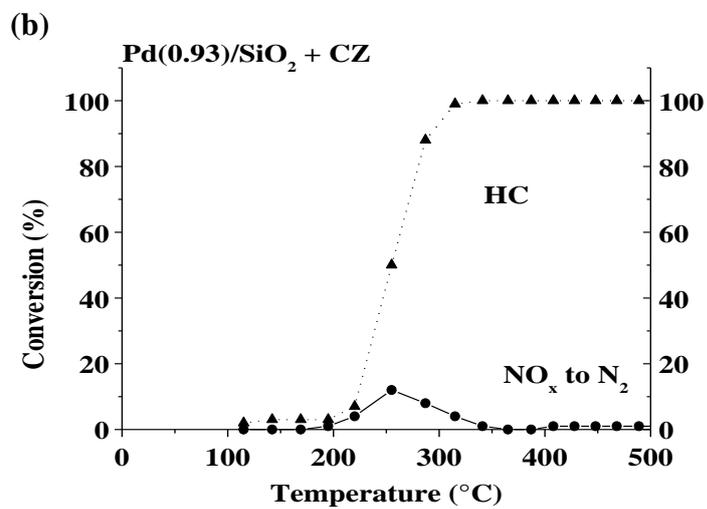
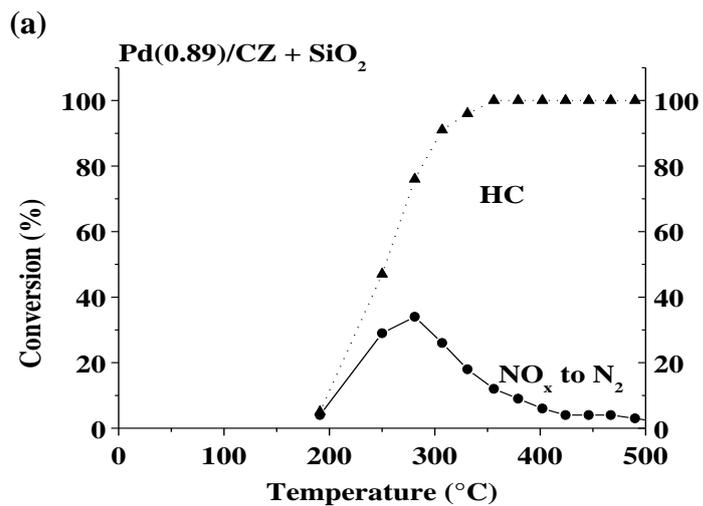
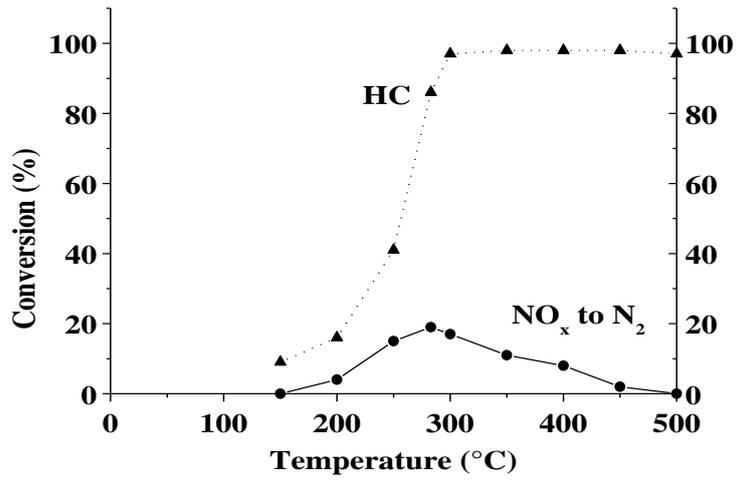


Fig. 10



**Fig. 11**



**Fig. 12**

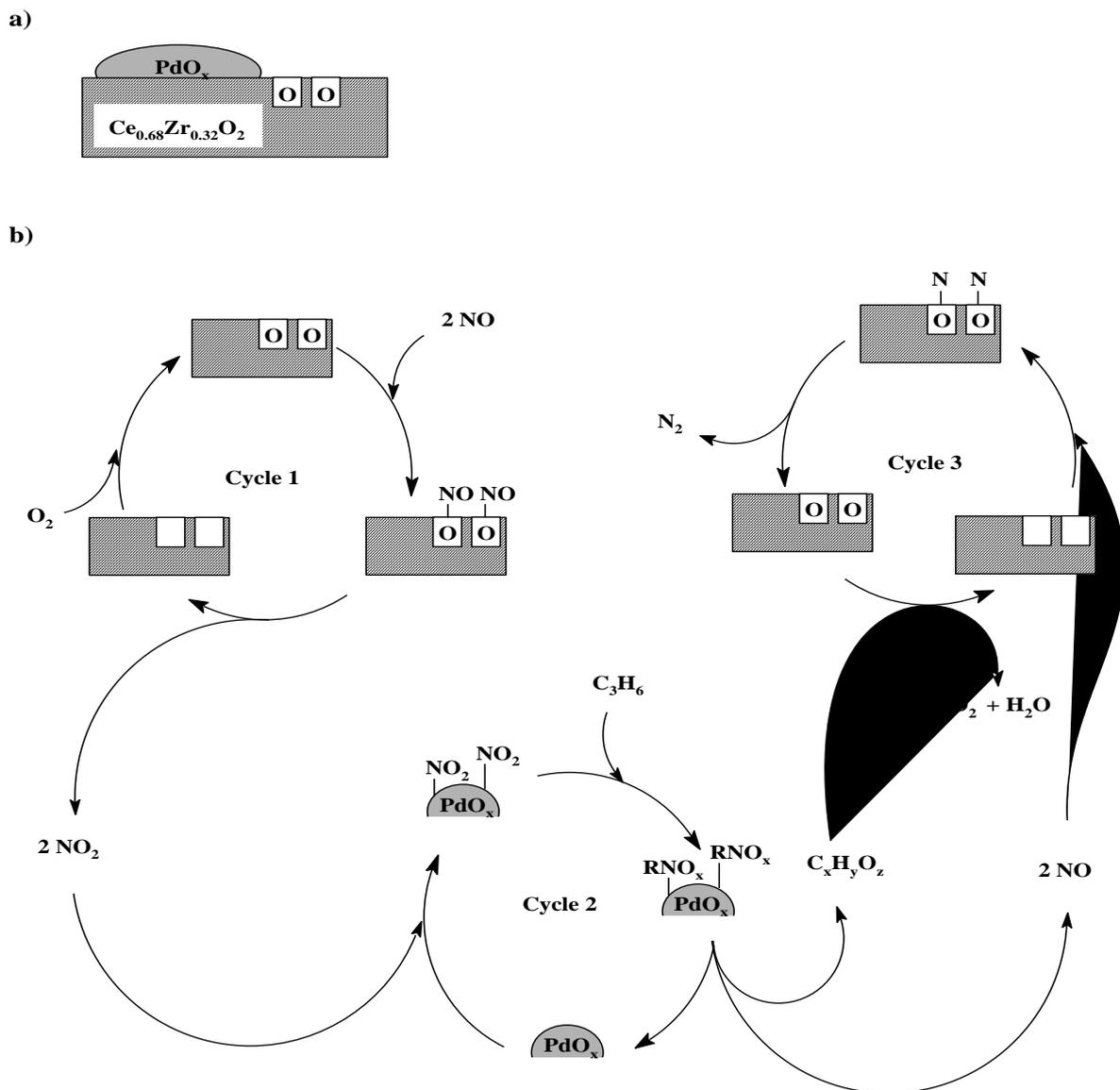


Fig. 13