

Surface reconstruction of supported Pd on LaCoO₃: Consequences on the catalytic properties in the decomposition of N₂O

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Abstract

This study deals with the catalytic decomposition of N₂O over noble metal based catalysts. The deposition of palladium on reducible supports such as LaCoO₃ leads to higher activity from temperature-programmed experiments in comparison with conventional supports such as alumina. Such a different catalytic behaviour cannot be completely explained by changes in the metal dispersion but also by the extent of the metal/support interaction. Interestingly, successive reductive (250 °C in H₂) and oxidative thermal treatments in the reactant mixture at high temperature enhance the conversion of N₂O particularly on perovskite support. Additional surface characterisations show a re-dispersion and the stabilisation of palladium species in unusual oxidation states which would originate a rate enhancement in the decomposition of N₂O.

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1. Introduction

Potential catalytic applications for perovskite materials ABO₃ have been previously reviewed [1]. Those materials can be attractive due to lower costs and flexibility of their composition since they can tolerate significant substitution and non-stoichiometry. The main drawback is usually related to their low specific surface area despite significant developments in the preparation procedures for obtaining solids exhibiting homogeneous compositions and high specific surface areas [2,3]. Also, those materials can be profitably used as support. The deposition of active phases, such as noble metals, may considerably enhance the overall activity due to cooperative effects between noble metals and the support. In this latter case, remarkable catalytic performances were obtained in the course of the reduction of NO by hydrogen in O₂ excess on 0.1 wt% Pt/La_{0.7}Sr_{0.2}Ce_{0.1}FeO₃ with significant rate and selectivity enhancement towards the transformation of NO into nitrogen below 200 °C [4,5]. It was found that this rate enhancement

may depend on the extent of metal/support interaction, i.e. on the metal dispersion, with the creation of highly active sites at the metal/support interface. Recently, Uenishi et al. [6] investigated the redox behaviour of palladium at start up in the perovskite-type structure LaFe_{0.95}Pd_{0.05}O₃ with Pd homogeneously distributed in the solid according to a sol–gel route for the catalyst synthesis. They also reported an interesting catalytic behaviour due to their self-regenerative function under cycling conditions with typical successive reductive and oxidative atmospheres. Under reductive conditions, isolated Pd species stabilised in the perovskite structure with unusual oxidation state +III and/or +IV segregated out onto the surface from the B-site at relatively low temperature then the nano-sized Pd⁰ particles re-oxidise under net oxidising conditions into Pd²⁺ at 200–300 °C. Successive formation of a solid solution occurs with an increase in temperature. Unfortunately, such reversible properties have been characterised essentially on highly-loaded Pd catalysts. Actually, a particular attention is paid towards the reduction of noble metal contents in the catalyst formulation or the development of alternative non-noble metal catalysts. According to those objectives, the use of sol–gel methods could not be a powerful procedure for optimising the surface concentration of noble metals particularly

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under net oxidising conditions with the concomitant formation of bulk solid solutions which hinders a significant fraction of noble metals. Nevertheless, the stabilisation of highly dispersed oxidic palladium species at high temperature with a partial suppression of thermal sintering process offers new perspectives to those materials particularly for high temperature catalytic applications.

Previous investigations dealing with the catalytic decomposition of N_2O (in the absence of reducing agent) pointed out the highest activity of Rh_2O_3 among the different transition metal oxides earlier investigated [7]. Rh_2O_3 is also more active than Rh^0 but the active sites involved in the decomposition have not been clearly elucidated. In addition, surface reconstructions may take place up to a certain limit of oxygen coverage leading to significant changes in the catalytic behaviour [8,9]. The usual strong oxygen inhibiting effect on the rate of N_2O decomposition can be lowered after deposition and stabilisation of oxidic Rh species in interaction with reducible supports such as La- and Pr-doped CeO_2 [10,11]. The segregation of well-dispersed RhO_x species on CeO_2 could be a key parameter [12]. In fact, oxygen from the dissociation of N_2O on Rh could diffuse on reducible supports then desorb with a lower activation barrier. The accumulation of chemisorbed O atoms and the competition for adsorption of N_2O and NO have to be taken into account from a practical viewpoint particularly for end-of-pipe technologies implemented for nitric acid plants. NO may originate the formation of stable nitrites and/or nitrates which could also have a strong detrimental effect on the catalytic performances. Taking into account those considerations, the stabilisation of well-dispersed PdO_x entities in strong interaction with the perovskite structure could be attractive for promoting the decomposition of N_2O and may represent an interesting practical issue for the replacement of Rh based catalysts. According to this objective, we have implemented an alternative strategy than that previously developed by Uenishi et al. [6] for the promotion of well-dispersed Pd/LaCoO_3 with lower Pd content and higher surface Pd concentration at the surface. In fact, it consists of a two-step procedure with a conventional wet impregnation of Pd precursor and appropriate successive reductive and oxidative thermal treatments. Those thermal treatments are accompanied with surface structural modifications which favour the re-dispersion of oxidic palladium species. According to this procedure, a significant rate enhancement is observed which cannot be related to weak interactions between PdO and LaCoO_3 but mainly to the occurrence of re-dispersion processes which could be governed by surface reconstructions of the perovskite structure during those successive thermal ageing. In that case, oxidic Pd species strongly interacting with LaCoO_3 would be stabilised in unusual oxidation states.

2. Experimental

2.1. Catalyst preparation and characterisation

The preparation procedure of LaCoO_3 ($20 \text{ m}^2 \text{ g}^{-1}$) was described elsewhere [13,14] using a so-called sol-gel method

involving a citrate route. Supported palladium catalysts on LaCoO_3 were prepared according to a classical wet impregnation route using palladium nitrate solutions with adjusted concentrations in order to obtain 1 wt% Pd. The impregnated samples were calcined in air at 400°C and then reduced at 250 or 500°C in pure H_2 overnight. H_2 titration measurements were performed at 100°C in order to minimise the formation of palladium hydrides in accordance with previous investigations [15]. The hydrogen uptake on pre-reduced samples in H_2 at 500°C , was 40.4 and $7.5 \mu\text{mol}$ per gram of catalyst respectively on $\text{Pd/Al}_2\text{O}_3$ and Pd/LaCoO_3 which corresponded to Pd dispersion of approximately 0.86 and 0.16 . Pd dispersion on LaCoO_3 pre-reduced at 250°C had not been considered due to overestimation since hydrogen spill-over effects during H_2 chemisorption measurements took place on reducible supports [16,17] depending on the reduction temperature particularly under mild conditions. Such an effect had to be taken into account at moderate reduction temperature.

Temperature-programmed reduction (TPR) was carried out in a Micromeritics Autochem II 2920 (5 vol% H_2/Ar). In situ X-ray diffraction (XRD) were performed using a Bruker D8 diffractometer equipped with a $\text{CuK}\alpha$ ($\lambda = 0.154 \text{ nm}$) radiation. The sample was in situ reduced under a flow of 3 vol% H_2 in He. The temperature was raised until the desired temperature (3°C min^{-1}) with a plateau of 1 h for data acquisition. X-ray photoelectron spectroscopy experiments (XPS) were performed using a Vacuum Generators Escalab 220XL spectrometer. A monochromatized aluminium source (1486.6 eV) was used for excitation. All binding energies were adjusted with the binding energy (BE) of C 1s (285.1 eV) as internal reference. Ex situ thermal activation treatments at atmospheric pressure were performed in a fixed-bed flow reactor and the aged samples were transferred in the analysis chamber under ultra high vacuum ($\sim 10^{-10}$ Torr) for XPS analysis. In situ experiments were carried out in a catalytic chamber coupled to the analyser.

2.2. Catalytic measurements

Temperature-programmed and steady state experiments were performed in a fixed-bed flow reactor using 0.7 g of catalyst in powder form. The total flow rate was 15 L h^{-1} , corresponding to a space velocity of approximately $10,000 \text{ h}^{-1}$. The reactant mixture was typically composed of 1000 ppm N_2O and 1000 ppm NO. The effluents were analysed with a μGC Varian 4900 chromatograph fitted with two thermal conductivity detectors and a Balzer mass spectrometer for the detection and the quantification of O_2 and NO_2 . Prior to quantification, reactants and products were separated on 5 \AA molecular sieve and Poraplot Q columns. The temperature was gradually increased during temperature-programmed experiments with a constant heating rate of 3°C min^{-1} .

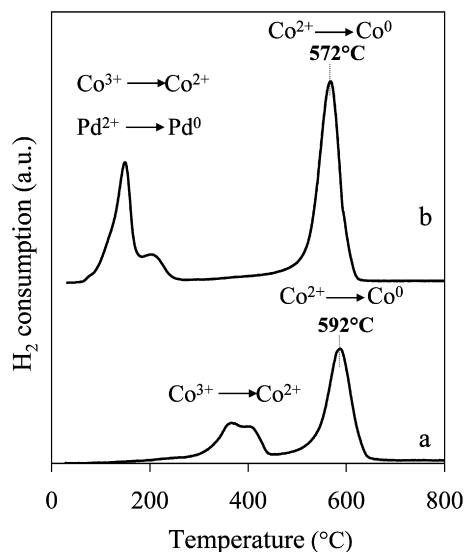


Fig. 1. Temperature-programmed reduction experiments ($10^\circ\text{C min}^{-1}$) under 5 vol% H_2 diluted in Ar on calcined LaCoO_3 (a) and reference PdO/LaCoO_3 (b).

3. Results

3.1. Bulk and surface characterisation of supported palladium catalysts

3.1.1. Freshly prepared catalysts

The reducibility of LaCoO_3 and PdO/LaCoO_3 has been investigated by H_2 temperature-programmed reduction. Results are reported in Fig. 1. The H_2 consumption profile vs temperature recorded on LaCoO_3 exhibits two consumption ranges highlighting a two-step reduction process. The low temperature range, between 200 and 450°C , is associated to the reduction of Co^{3+} into Co^{2+} according to the calculation of the atomic H/Co ratio equal to 1.04 ± 0.05 . The high temperature consumption range above 450°C , with $\text{H/Co} = 1.96 \pm 0.09$, corresponds to an extensive reduction of Co^{2+} to metallic Co particles. As observed in Fig. 1b, a significant shift towards lower temperatures is observed in the presence of palladium which suggests that the partial reduction of Co^{3+} into Co^{2+} could be catalysed by the presence of metallic palladium particles.

Such observations are in qualitative agreement with in situ XRD measurements on LaCoO_3 under reductive atmosphere (3 vol% H_2 in He). XRD patterns in Fig. 2 reveal a significant shift of the most intense X-ray line at $2\theta = 32.9^\circ$ ascribed to the rhomboedral structure of LaCoO_3 up to 300°C due to the partial reduction of Co(III) located in the B site of the perovskite structure. A subsequent increase in temperature at 500°C leads to a strong attenuation and a complete disappearance of X-ray lines characteristic of LaCoO_3 . Correlatively, an additional contribution develops at $2\theta = 29.9^\circ$ which characterises La_2O_3 . The reductive pre-treatment induced effect on the surface properties of LaCoO_3 has been investigated by XPS. As shown in Fig. 3, the Co $2p_{3/2}$ spectra recorded on calcined LaCoO_3 and after reduction at 500°C are respectively located at 780.0 and 778.1 eV. An intermediate BE value is obtained after reduction

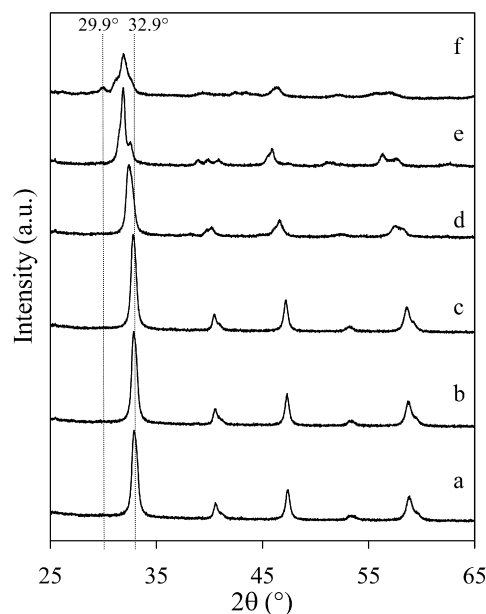


Fig. 2. In situ XRD analysis of LaCoO_3 during reductive thermal treatment in 3 vol% H_2 diluted in He: calcined LaCoO_3 (a), 100°C (b), 200°C (c), 300°C (d), 400°C (e), 500°C (f).

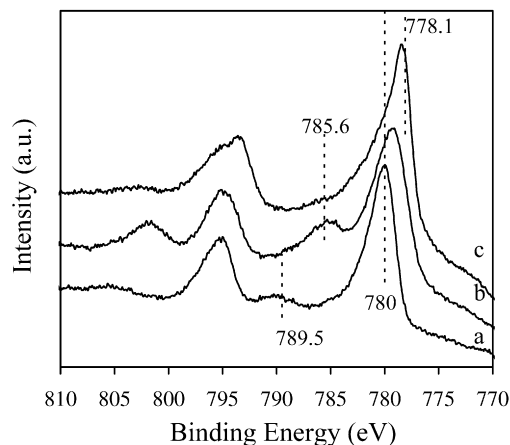


Fig. 3. XPS Co $2p$ spectra recorded after different in situ reductive thermal treatments (10 vol% H_2 in N_2): calcined LaCoO_3 (a), pre-reduction at 300°C (b), pre-reduction at 500°C (c).

in mild conditions at 300°C accompanied with the development of the characteristic shake up structure at 785.6 eV which evidences the presence of Co^{2+} . Semi-quantitative analysis in Table 1 indicates a complete surface reduction of Co^{3+} to Co^{2+} at 300°C while Co^0 and Co^{2+} coexist after reduction at 500°C . Prior to reaction, PdO/LaCoO_3 was pre-activated under isothermal conditions in pure H_2 overnight at 250 or 500°C . As indicated in Table 2, pre-reduction in mild conditions at 250°C leads to a complete reduction of PdO into Pd^0 with BE value for Pd $3d_{5/2}$ core level characteristic of metallic Pd particles [18] whereas the bulk structural properties of LaCoO_3 are preserved with complete reduction of Co^{3+} into Co^{2+} at the surface in accordance with previous XPS measurements reported in Table 1. On the other hand, an extensive bulk reduction of the perovskite into CoO_x and La_2O_3 was observed at 500°C yielding $\text{Pd}^0/\text{CoO}_x/\text{La}_2\text{O}_3$.

Table 1
Changes in oxidation state and surface concentration of oxidic cobalt species in LaCoO₃ after exposure to reductive thermal treatments

Preactivation thermal treatment	BE (eV) ^a Co 2p _{3/2} core level	Relative surface composition (%)		
		Co ³⁺	Co ²⁺	Co ⁰
Calcined LaCoO ₃	780	100	–	–
Pre-reduced in H ₂ at 300 °C	779.7	–	100	–
Pre-reduced in H ₂ at 500 °C	778.1	–	40	60

^a BE—binding energy.

Table 2
Changes in surface composition of Pd supported on LaCoO₃ under controlled oxidative and reductive atmospheres

Thermal pretreatment	XPS analysis					H ₂ chemisorption ^a	
	BE (eV) ^b Pd 3d _{5/2}	Peak width (eV)	Relative surface atomic composition ^c			H ₂ uptake (μmol g ⁻¹)	D ^d
			Pd/La	Co/La	O/La		
Calcination in air at 400 °C	336.8	1.6	0.04	0.45	2.9		
Reduction in H ₂ at 250 °C	335.4	1.6	0.04	0.60	3.6		
Reduction in H ₂ at 500 °C	335.1	1.6	0.04	0.62	2.4	7.5	0.16
Reduction at 250 °C and ageing in N ₂ O/NO at 250 °C	337.0	3.8	0.05	0.46	2.7	8.0	0.17
Reduction at 250 °C and ageing in N ₂ O/NO at 500 °C	337.2	1.6	0.11	0.63	2.7	4.95	0.105
Reduction at 500 °C and ageing in N ₂ O/NO at 400 °C	337.3	2.0	0.03	0.81	3.6	5.0	0.11

^a Performed at 100 °C.

^b BE—binding energy.

^c Relative accuracy equal to ±20%.

^d Metal dispersion.

3.1.2. Influence of the thermal ageing under reactive conditions on surface properties of pre-reduced supported Pd on LaCoO₃

According to the nature of the activation thermal treatment and successive thermal ageing under oxidative conditions, metallic or oxidic Pd species can be segregated as Pd(II) into PdO or in different chemical environments depending on the extent of interaction with the support and related changes in structural properties. Under reactive conditions, in the presence of NO and N₂O, different chemical processes can occur on pre-reduced catalysts at 500 °C associated to bulk and surface re-oxidation as well as catalytic reactions involving both molecules on re-oxidised surfaces. Pre-reduced catalysts have been aged in the reactive mixture at high temperature overnight in order to accelerate bulk re-oxidation processes and to characterise the surface properties involved in the catalytic decomposition of NO and N₂O.

3.1.2.1. Bulk characterisation XRD patterns recorded after ageing in 1000 ppm NO and 1000 ppm N₂O diluted in He overnight at 500 °C are reported in Fig. 4. Clearly, the rhomboedral structure prevails on the aged samples previously reduced at 250 °C with characteristic X-ray lines located at the same position in 2θ as those observed on the reference PdO/LaCoO₃ sample. On the contrary, the perovskite structure is not evidenced on the aged sample initially reduced at 500 °C with X-ray lines characteristic of La₂O₃. Bulk Co species are also detectable at 2θ = 37° associated with the segregation of Co₃O₄. H₂-TPR experiments were performed on the aged catalysts in order to examine changes in the reducibility of oxidic cobalt species after thermal ageing. The effluents during TPR experiments were simultaneously analysed by mass spectrometry.

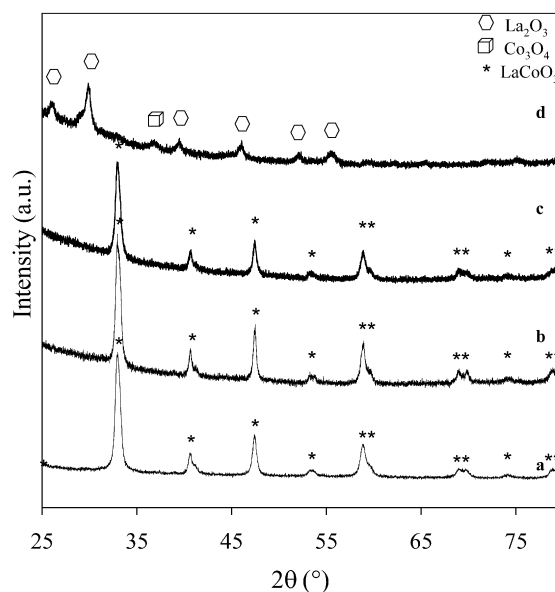


Fig. 4. Ex situ XRD analysis of Pd/LaCoO₃ catalysts after successive pre-activation treatment and thermal ageing under reactive conditions in the presence of 1000 ppm NO and 1000 ppm N₂O: calcination at 400 °C (reference PdO/LaCoO₃) (a), pre-reduced at 250 °C and aged under N₂O/NO at 500 °C (b), pre-reduced at 250 °C and aged under N₂O/NO at 250 °C (c), pre-reduced at 500 °C and aged under N₂O/NO at 400 °C (d).

try. H₂ consumption profiles versus temperature are collected in Fig. 5. As observed the reducibility of oxidic Co species after ageing strongly depends on the temperature of the pre-reductive thermal treatment in H₂. Under mild conditions, with a reduction temperature of 250 °C, the shape of the profiles approximately mimics that previously reported on a reference PdO/LaCoO₃ with two distinct H₂ consumption ranges corre-

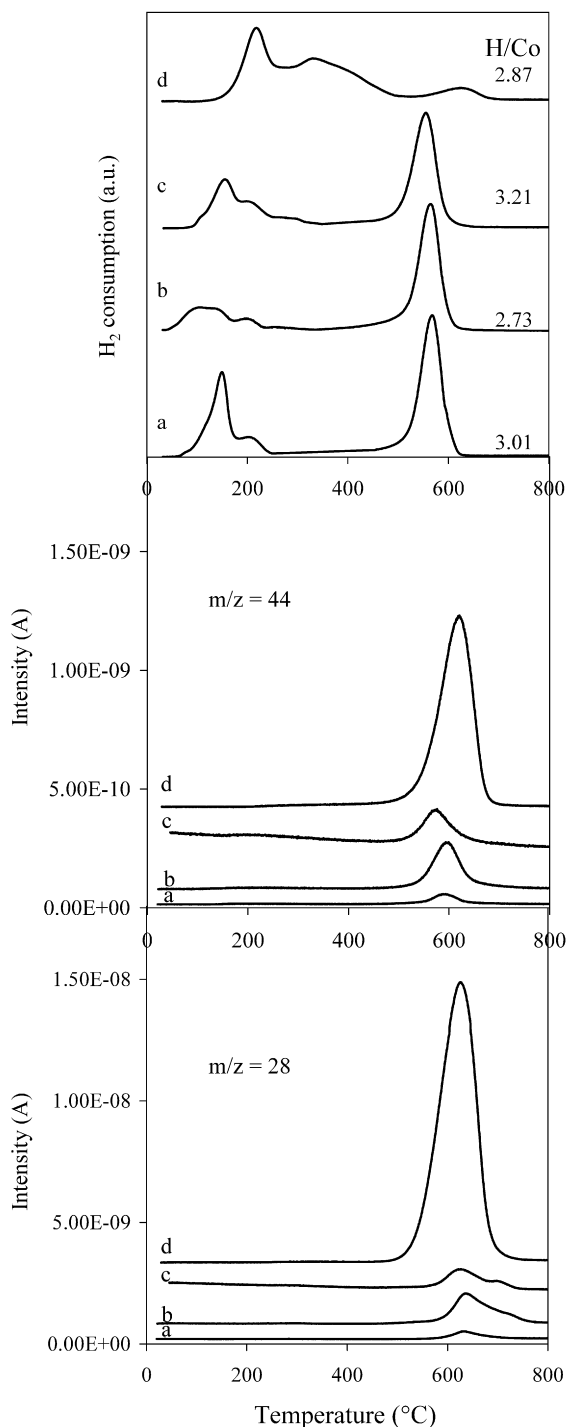


Fig. 5. Temperature-programmed reduction experiments under 5 vol% H_2 diluted in Ar on aged-samples under reactive conditions in the presence of 1000 ppm NO and 1000 ppm N_2O : H_2 -consumption profiles recorded on reference PdO/LaCoO₃ (a); pre-reduced at 250 °C and aged at 250 °C (b), pre-reduced at 250 °C and aged at 500 °C (c), pre-reduced at 500 °C and aged at 400 °C (d). Simultaneous analysis of the effluents by mass spectrometry with $m/z = 28$ associated to the presence of N_2 and CO and $m/z = 44$ associated to the formation of CO_2 and N_2O in the gas phase.

sponding to a two-step reduction process with the intermediate formation of Co^{2+} species. On the other hand, such a comparison cannot be achieved after pre-reduction in severe conditions at 500 °C with a strong attenuation of the high temperature H_2

consumption range and the development of a broad signal between 150 and 500 °C. Such an observation is well in agreement with XRD measurements which did not show the restoration of the rhomboedral structure of LaCoO₃ after successive reductive and ageing thermal treatments respectively at 500 and 400 °C. The calculation of atomic H/Co ratio, equal to 2.87, is slightly higher than the theoretical one for the bulk reduction of Co_3O_4 . Coming back to Fig. 5, b and c, relative to pre-reduced samples in mild conditions ($T = 250$ °C) then aged under reactive mixture at 250 and 500 °C, respectively, subsequent comparisons with the reference PdO/LaCoO₃ provides interesting information relative to changes of the reducibility of oxidic palladium and cobalt species. A particular attention is focused on the low temperature H_2 consumption range in Fig. 5b. As exemplified, the H_2 consumption starts at lower temperature on the aged sample at 250 °C than on the reference PdO/LaCoO₃. On the other hand, such a low temperature process strongly attenuates on the aged sample at 500 °C (see Fig. 5c). Such differences will be discussed more extensively in the light of additional surface characterisation. The calculation of the atomic H/Co ratio leads to an unexpectedly low value of 2.73 for the aged sample in mild conditions at 250 °C in comparison with the theoretical value of 3 corresponding to the complete reduction of LaCoO₃ into metallic Co species and La₂O₃. Such a low value may underline an incomplete re-oxidation of the catalyst during thermal ageing. On the other hand, the value recorded after ageing at 500 °C exceeds the theoretical one. Mass spectrometry analysis provides complementary information. As exemplified in Fig. 5, CO_2 and N_2O , associated to the relative mass $m/z = 44$, and CO and N_2 , corresponding to $m/z = 28$, are detected above 500 °C. Their presence could be explained by the accumulation of carbonates during contact in air at room temperature and/or by the accumulation of nitrate and nitrite compounds during thermal ageing. Their reduction in the presence of H_2 at high temperature above 500 °C may take place and explain the extra consumption of hydrogen. It is worthwhile to note that the production of carbon and/or nitrogen-containing products is more pronounced on the pre-reduced Pd/LaCoO₃ at 500 °C and aged at 400 °C and coincides with the high temperature H_2 consumption signal.

3.1.2.2. Surface characterisation XPS analysis provides additional data relative to changes in the oxidation state and chemical environment of palladium and cobalt in comparison with PdO/LaCoO₃. Co 2p spectra recorded on the aged samples are listed in Fig. 6. As illustrated no significant change is discernable according to the temperature of the pre-reduction and ageing processes. The binding energy value of the Co 2p_{3/2} core level associated with the shake up structure respectively at 780.0 and 789.5 eV essentially characterise the presence of Co^{3+} . The presence of Co^{2+} cannot be ruled out particularly on the pre-reduced and aged sample respectively at 500 and 400 °C associated to the segregation of Co_3O_4 . As exemplified in Fig. 6b, the shake up structure relative to Co^{2+} at 785.6 eV may contribute to the overall signal. Fig. 7 shows Pd 3d spectra recorded after different ex situ thermal treatments under controlled atmospheres. The photopeak Pd 3d_{5/2} recorded on the

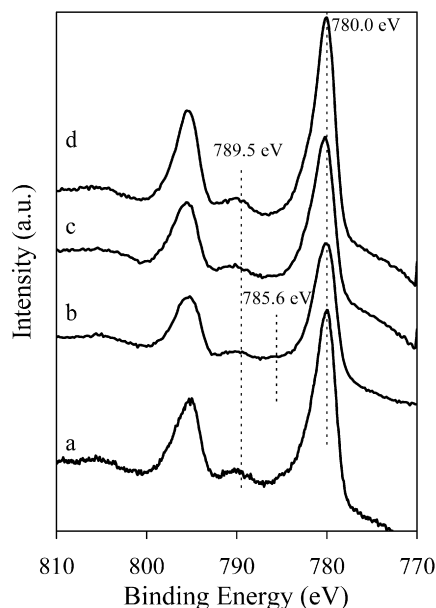


Fig. 6. Co 2p spectra recorded on aged Pd/LaCoO₃ catalysts under reactive conditions (1000 ppm NO and 1000 ppm N₂O): reference PdO/LaCoO₃ (a), pre-reduced at 500 °C and aged at 400 °C (b), pre-reduced at 250 °C and aged at 250 °C (c), pre-reduced at 250 °C and aged at 500 °C (d).

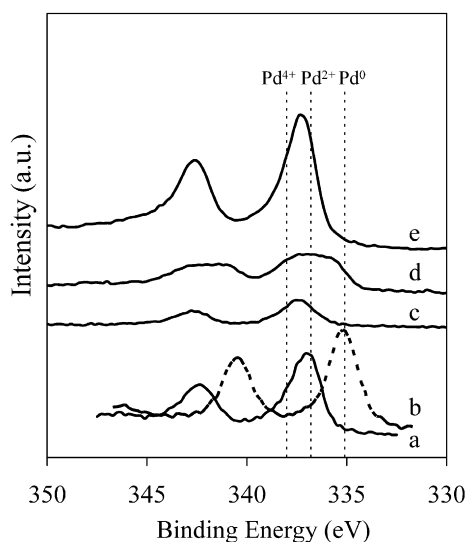
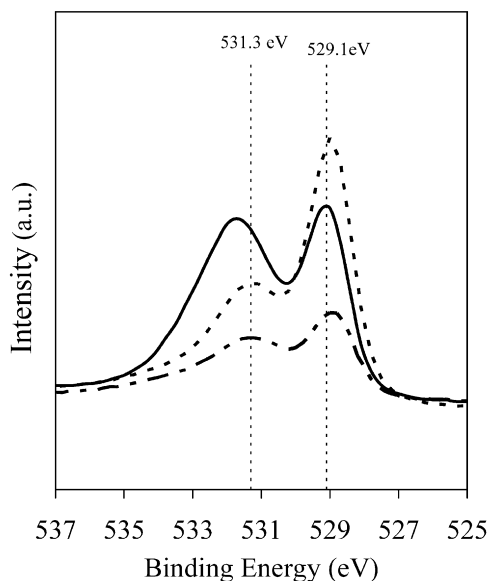


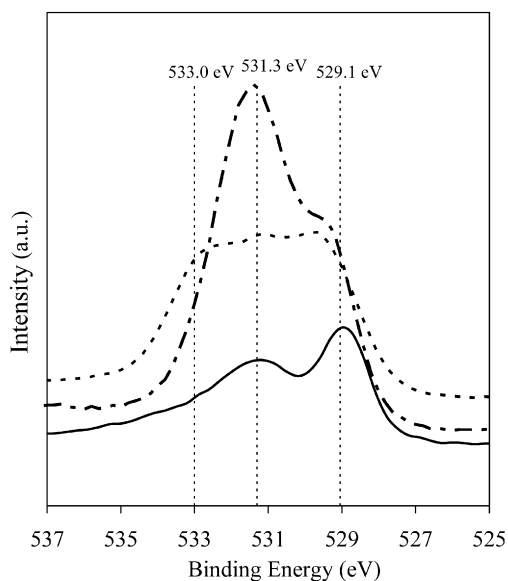
Fig. 7. Pd 3d spectra recorded on Pd/LaCoO₃ catalysts after various ex situ thermal ageing: calcination at 400 °C (reference PdO/LaCoO₃) (a), pre-reduced at 500 °C (b), pre-reduced at 500 °C and aged at 400 °C under N₂O/NO (c), pre-reduced at 250 °C and aged at 250 °C under N₂O/NO (d), pre-reduced at 250 °C and aged at 500 °C under N₂O/NO (e).

calcined sample in air at 400 °C located at 336.8 eV mainly characterises Pd²⁺ probably into PdO. The current value earlier reported for PdO deposited on conventional supports such as alumina are slightly lower around 336.2 eV [18]. Such a shift could be significant and may reflect a more extensive interaction between Pd²⁺ species on LaCoO₃ than on alumina. A shift towards lower BE values near 335.1 eV is observed after reductive thermal treatment in H₂ at 500 °C which characterises the presence of metallic Pd particles. Similar information can be obtained after reduction at 250 °C (see Table 2). Thermal

ageing in 1000 ppm NO and 1000 ppm N₂O at 250 °C leads to a significant broadening of the Pd 3d_{5/2} photopeak which highlights the segregation at the surface of different palladium species stabilised in different oxidation states, essentially Pd⁰ and Pd²⁺ (Fig. 7d). A more extensive surface oxidation takes place with an increase in the thermal ageing temperature at 500 °C associated with a shift of the Pd 3d_{5/2} at 337.2 eV which only characterises the presence of Pd²⁺. The slightly higher value than that obtained on PdO/LaCoO₃ may reflect different chemical environment for Pd²⁺ species. Similar observations were reported by Uenishi et al. [6] with the observation of oxidic palladium species exhibiting binding energy values between those currently reported for Pd²⁺ in PdO and Pd⁴⁺ in PdO₂, respectively, equal to 336.2 and 338 eV [19]. Those authors suggested the stabilisation of unusual Pd(III) species assisted by the perovskite structure. Interestingly, a significant increase in intensity signal is discernible in comparison with that obtained on the reference PdO/LaCoO₃ which indicates a higher surface concentration of palladium species after successive oxidative/reductive thermal treatments. Spectral features are summarised in Table 2 with semi-quantitative analysis. Clearly, the surface Pd composition is higher after successive reduction and thermal ageing treatment respectively at 250 and 500 °C. Regarding the pre-reduced sample at 500 °C, a drop in surface Pd composition is observed. Parallel to this observation a significant increase in surface Co concentration is observed which cannot be related to the surface reconstruction of LaCoO₃ but more probably to the segregation of Co₃O₄ according to XRD observations. The examination of the photopeak O 1s provides additional arguments. As observed in Figs. 8a and 8b, two contributions arise at 529.1 ± 0.2 eV and 531.3 ± 0.2 eV on the O 1s photopeak which have been previously assigned to oxygen species from the perovskite structure and OH groups on the surface [20,21]. Earlier investigations [22,23] revealed changes in the relative intensity of both contributions according to the extent of reduction. Our observations are in qualitative agreement with those previous findings with an increase of OH groups after reduction and the development of the 529.1 eV contribution after re-oxidation except on the pre-reduced sample at 500 °C since an additional contribution appears at 533 eV (see Fig. 8b). Complementary observations can be provided from the examination of the N 1s photopeak. As exemplified in Fig. 9, XPS spectra are dominated by two contributions on the overall signals at 403.7 and 407.3 eV previously assigned to nitrites and nitrates species respectively [18,24]. Both contributions observable prior reduction in H₂ on PdO/LaCoO₃ attenuate on aged catalysts previously reduced under mild conditions at 250 °C. On the other hand they intensify on the aged sampled previously reduced in severe conditions at 500 °C. Such an observation is in relative good agreement with H₂-TPR experiments (see Fig. 5) with the simultaneous formation N-containing products in the outlet gas mixture above 500 °C. This formation more accentuated on the pre-reduced and aged sample, respectively, at 500 and 400 °C could be associated to reduction of nitrates and nitrites in the presence of hydrogen. Consequently the shoulder on the O 1s spectra at 533 eV could be partly explained by



(a)



(b)

Fig. 8. O 1s spectra recorded on Pd/LaCoO₃ catalysts: (a) fresh catalyst (reference PdO/LaCoO₃) (---), pre-reduced under hydrogen at 250 °C and aged under inlet mixture at 500 °C (· · · ·), pre-reduced under hydrogen at 250 °C and aged under inlet mixture at 250 °C (—); (b) fresh catalyst (—), pre-reduced under hydrogen at 500 °C (---), pre-reduced under hydrogen at 500 °C and aged under inlet mixture at 400 °C (· · ·).

the accumulation of strongly chemisorbed nitrites and nitrates from NO adsorption and successive surface reactions between those chemisorbed NO and O atoms leading to the formation of nitrates. One cannot rule out the contribution of carbonates species on the O 1s spectra as previously observed by Natile et al. [21]. Nevertheless no noticeable change in intensity of the photopeak C 1s was observed according to thermal ageing conditions (results not shown) which could explain changes in the intensity of relative masses $m/z = 44$ and 28 due to the decomposition and/or reduction of carbonates (see Fig. 5).

H₂ chemisorption measurements were performed on aged samples in order to examine changes in the metal dispersion.

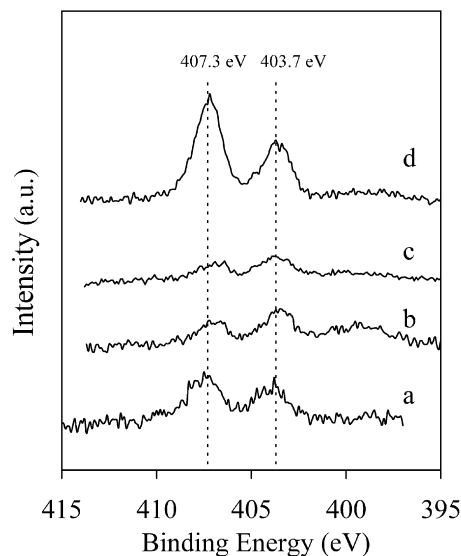


Fig. 9. N 1s spectra recorded on Pd/LaCoO₃ catalysts: (a) fresh catalyst (reference PdO/LaCoO₃); (b) pre-reduced under hydrogen at 250 °C and aged under inlet mixture at 250 °C; (c) pre-reduced under hydrogen at 250 °C and aged under inlet mixture at 500 °C; (d) pre-reduced under hydrogen at 500 °C and aged under inlet mixture at 400 °C.

Experiments were achieved at 100 °C to minimise the formation of bulk hydride species [15]. In all cases, the aged samples were reduced at 500 °C for further comparison with the reference PdO/LaCoO₃. The values of the metal dispersion are reported in Table 2. As observed a loss of metal dispersion is distinguishable after ageing except for the reduced and aged sample under mild conditions ($D = 0.17$). The comparison of XPS and H₂ titration results obtained on the pre-reduced and aged samples respectively at 250 and 500 °C reveals some divergences. As indicated in Table 2 this sample exhibits the highest atomic Pd/La ratio and the lowest metal dispersion. As a matter of fact, such a comparison could not be controversial since XPS analysis does not concern the topmost layer but provides an average composition on a depth representing approximately ten mono-layers. Also an additional aspect has to be taken into account suggested by TPR experiments which show different reducibility according to the temperature of the thermal ageing process. In this sense, the highest metal dispersion obtained after ageing at 250 °C could be correlated to the development of the low H₂ consumption range in Fig. 5b and associated to the segregation of well-dispersed PdO particles [25]. Now, different explanation could be proposed concerning to disappearance of those species on the aged sample at 500 °C which may explain the loss of metal dispersion. Thermal sintering processes may occur but a more extensive redispersion phenomenon could also be accounted for with a partial incorporation oxidic Pd species inside the perovskite structure. Such a process could generate less reducible oxidic palladium species and then explain the underestimation of the metallic palladium dispersion. Such an explanation seems in good agreement with the shift of the Pd 3d_{5/2} core level towards higher values which suggests changes in the chemical environment of oxidic palladium species (see Fig. 7).

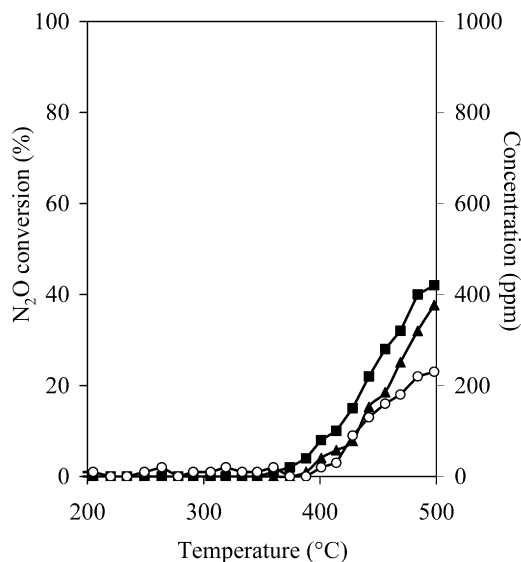
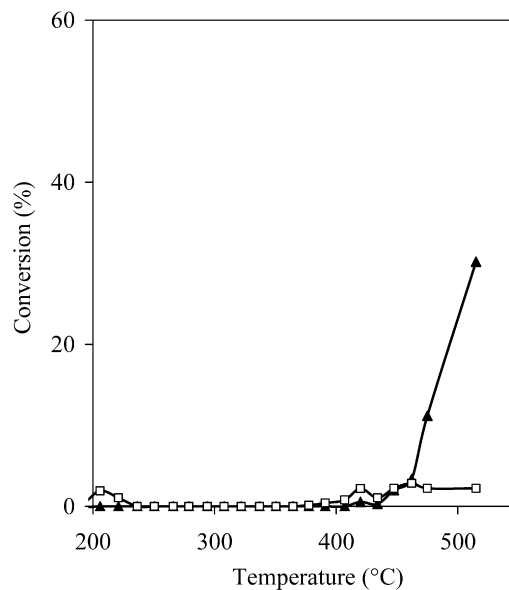


Fig. 10. Temperature-programmed experiment of the catalytic decomposition of N_2O to N_2 and O_2 on $\text{Pd}/\text{Al}_2\text{O}_3$ pre-reduced at 250°C and 1000 ppm N_2O diluted in He: N_2O conversion (\blacktriangle), N_2 concentration (\blacksquare), O_2 concentration (\circ).

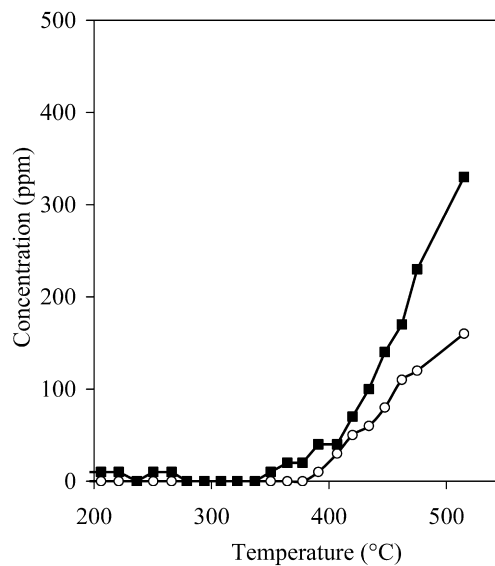
3.2. Catalytic performances in the decomposition of N_2O on pre-reduced Pd catalysts supported on Al_2O_3 and LaCoO_3

3.2.1. Freshly prepared $\text{Pd}/\text{Al}_2\text{O}_3$ and Pd/LaCoO_3

Preliminary experiments were performed in the absence of NO on reference $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts. The conversion profile and the amount of N_2 and O_2 produced from the decomposition vs temperature are reported in Fig. 10. The decomposition of N_2O is accompanied with the simultaneous production of N_2 and O_2 . N_2O conversion starts at 400°C and then reaching a maximum at 500°C of approximately 40%. A significant shift of the N_2O conversion curve towards higher temperature is observable in the presence of NO (see Figs. 11a and 11b) which underlines an inhibiting effect of NO on the rate of N_2O conversion. A weak conversion of NO is noticeable in the whole temperature range of the study which does not exceed 2.5%. Different observations have been obtained on pre-reduced Pd/LaCoO_3 at 250°C with the occurrence of two conversion ranges in Fig. 12. The low temperature conversion range, with no significant observation of oxygen in the gas phase, can be assigned to the re-oxidation of the solid by N_2O . The catalytic decomposition takes place above 400°C . It is worthwhile to note that a more extensive conversion than that recorded on $\text{Pd}/\text{Al}_2\text{O}_3$ is obtained of approximately 90% at 500°C . Complex features are observable in the presence of NO (results not shown) since N_2O and NO compete for the re-oxidation. In that case a poor production of oxygen was observed above 470°C which signifies a strong detrimental effect of NO on the catalytic decomposition of N_2O . Similar temperature-programmed experiments in the presence of NO and N_2O has been performed on LaCoO_3 and $\text{PdO}/\text{LaCoO}_3$ calcined in air at 400°C . In that case, no surface re-oxidation takes place. As observed in Figs. 13a and 13b, a slightly lower N_2O conversion is observed than that obtained on pre-reduced Pd/LaCoO_3 then re-oxidised under reactive mixture, starting



(a)



(b)

Fig. 11. Temperature-programmed experiment of the catalytic decomposition of N_2O to N_2 and O_2 in the presence of NO on $\text{Pd}/\text{Al}_2\text{O}_3$ pre-reduced at 250°C and 1000 ppm N_2O and 1000 ppm NO diluted in He: (a) N_2O conversion (\blacktriangle), NO conversion (\square); (b) N_2 concentration (\blacksquare), O_2 concentration (\circ).

at the same temperature of 400°C but reaching 60% against 90% in the absence of NO. Parallel to this observation a weak NO conversion occurs between 200 and 380°C which is not correlated to the formation of products in the gas phase (see Fig. 13b). Such observations could be related by the stabilisation of nitrates and/or nitrites species on $\text{PdO}/\text{LaCoO}_3$. Further comparison with calcined LaCoO_3 leads to comparable activity in N_2O conversion. The main difference is associated to a significant attenuation of NO conversion.

3.2.2. On aged supported palladium catalysts

The conversion profiles of N_2O vs temperature in the presence of NO on pre-reduced catalysts then aged overnight

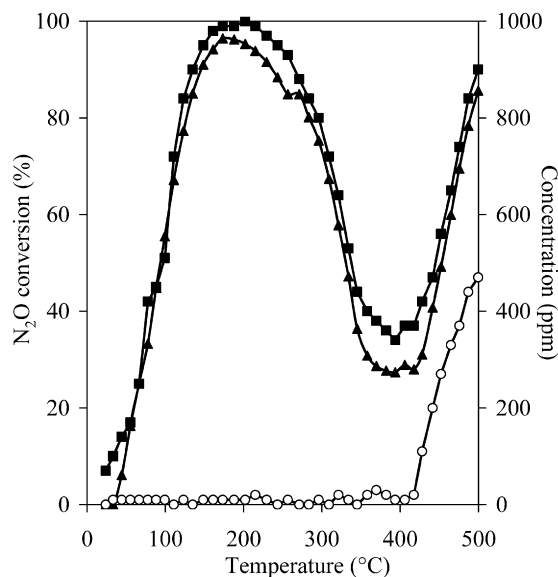


Fig. 12. Temperature-programmed experiment of the catalytic decomposition of N_2O to N_2 and O_2 on Pd/LaCoO_3 pre-reduced at 250°C and 1000 ppm N_2O diluted in He: N_2O conversion (\blacktriangle), N_2 concentration (\blacksquare), O_2 concentration (\circ).

under reactive conditions at 250 and 500°C are reported in Fig. 14a. The correlative formation of oxygen in the gas phase in Fig. 14b emphasises the fact that the catalytic decomposition of N_2O predominantly occurs with no significant involvement of side reactions associated to bulk re-oxidation process of the solid. As exemplified, significant changes in the activity are observable. A qualitative estimation of the overall activity in the decomposition of N_2O can be obtained from the T_{50} (temperature corresponding to 50% N_2O conversion) which increases according to the following sequence: PdO/LaCoO_3 ($T_{50} = 481^\circ\text{C}$) = Pd/LaCoO_3 Red. 500°C –Ox. 400°C ($T_{50} = 480^\circ\text{C}$) < LaCoO_3 Red. 250°C –Ox. 500°C ($T_{50} = 465^\circ\text{C}$) < Pd/LaCoO_3 Red. 250°C –Ox. 250°C ($T_{50} = 460^\circ\text{C}$) < Pd/LaCoO_3 Red. 250°C –Ox. 500°C ($T_{50} = 433^\circ\text{C}$). This comparison leads to different comments. First, a better catalytic activity in decomposition of N_2O is observed on LaCoO_3 after pre-reduction and ageing than on the calcined LaCoO_3 (see Fig. 13a). However the most interesting observation is related to the significant rate enhancement observed on Pd/LaCoO_3 Red. 250°C –Ox. 500°C with N_2O conversion starting above 350°C . On the contrary the loss of the perovskite structure after pre-reduction at high temperature has a detrimental effect on the activity. Also the reference PdO/LaCoO_3 exhibits a lower activity which underlines that surface and bulk reconstructions which take place during thermal ageing under reactive conditions lead to different surface properties than those obtained on the reference PdO/LaCoO_3 catalyst with the promotion of cooperative effects between oxidic palladium species and the perovskite which may originate such an extra conversion. The calculation of the apparent activation energy from temperature experiments are reported in Table 3. They have been compared to the intrinsic rates roughly estimated from conversion values recorded at 460°C and according to the number surface

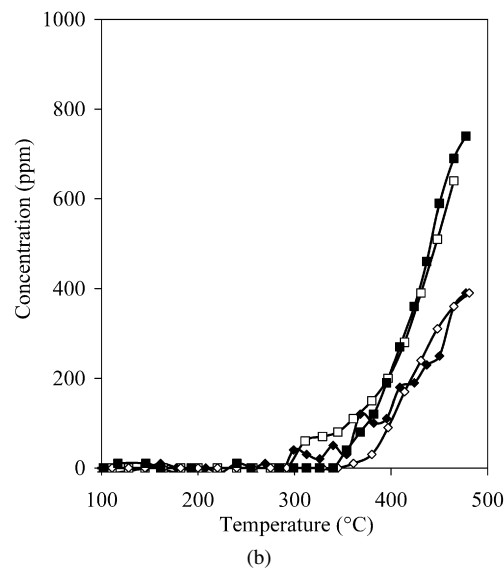
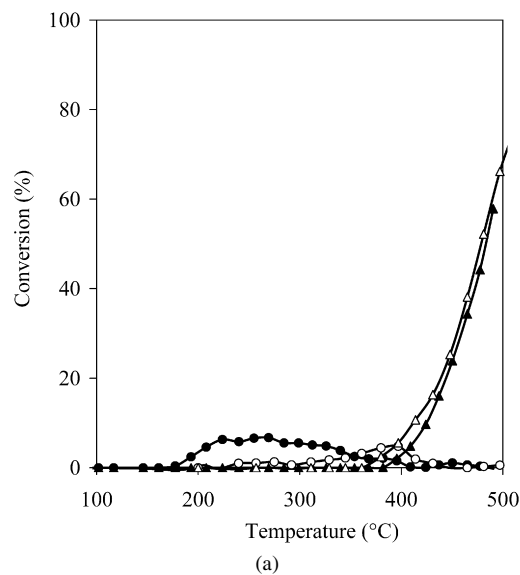


Fig. 13. Temperature-programmed experiments of the catalytic decomposition of N_2O to N_2 and O_2 in the presence of NO on calcined LaCoO_3 (open symbols) and PdO/LaCoO_3 (full symbols)–1000 ppm N_2O and 1000 ppm NO diluted in He: (a) N_2O conversion (\triangle , \blacktriangle), NO conversion (\circ , \bullet); (b) N_2 concentration (\square , \blacksquare), O_2 concentration (\diamond , \blacklozenge).

atoms calculated from H_2 titration. As observed significant changes occur according to the nature of the support. Clearly, higher values for the apparent activation energy (E_{app}) are obtained on alumina based catalysts which agree with lower intrinsic rate than that estimated on perovskite based catalysts. The comparable values obtained for E_{app} and the intrinsic rate on the reference $\text{PdO/Al}_2\text{O}_3$ and after pre-reduction in pure H_2 at 250°C of respectively 93 ± 5 and 89 ± 5 kJ mol^{-1} , with variation within the margin of error, suggest that when the decomposition of N_2O takes place at relatively high temperature (up to 400°C), the catalyst sample exhibits quasi-similar surface properties irrespective of the nature of the pre-activation thermal treatment. Now regarding Pd supported on perovskite, significant lower values have been calculated for E_{app} between 42 ± 3 and 55 ± 3 kJ mol^{-1} for the ref-

Table 3
Influence of thermal ageing on the catalytic performances of Pd/Al₂O₃ and Pd/LaCoO₃ catalysts in the decomposition of N₂O

Catalyst	Thermal treatment	T ₅₀ (°C)	N ₂ O conversion ^a at 460 °C	Intrinsic rate ^b (mol h ⁻¹ Pd _{surf} ⁻¹)	E _{app} (kJ mol ⁻¹) ^c
PdO/Al ₂ O ₃	Calcination in air at 400 °C	510	0.15	1.6	93 ± 5
Pd/Al ₂ O ₃	Reduction in H ₂ at 250 °C	520	0.04	0.4	89 ± 5
PdO/LaCoO ₃	Calcination in air at 400 °C	481	0.32	19	55 ± 3
Pd/LaCoO ₃	Reduction in H ₂ at 250 °C ageing in N ₂ O/NO at 250 °C	460	0.48	26	51 ± 3
Pd/LaCoO ₃	Reduction in H ₂ at 250 °C ageing in N ₂ O/NO at 500 °C	433	0.74	66	42 ± 3
Pd/LaCoO ₃	Reduction in H ₂ at 500 °C ageing in N ₂ O/NO at 400 °C	480	0.30	25	52 ± 3

^a Calculated at 460 °C from TPR experiments.

^b Calculated at 460 °C from the number of metallic Pd sites calculated from H₂ titration measurements.

^c Apparent activation energy.

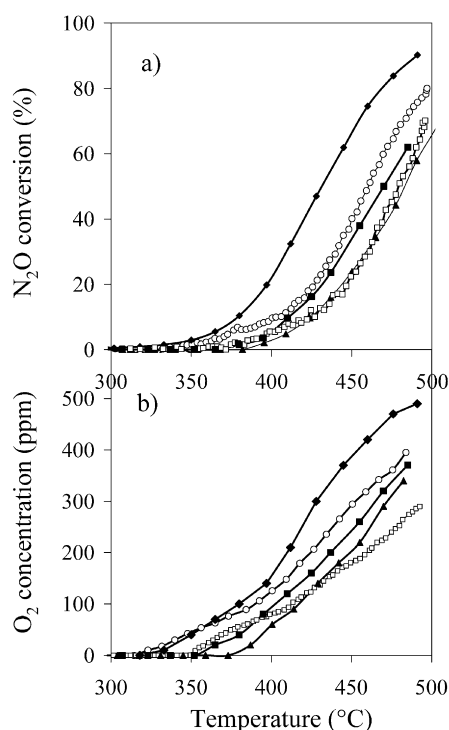


Fig. 14. Ageing induced effect on the catalytic performances in the decomposition of N₂O in the presence of NO on LaCoO₃ pre-reduced at 250 °C and aged under N₂O/NO at 500 °C (■) and on freshly-prepared PdO/LaCoO₃ calcined at 400 °C (▲); then pre-reduced at 250 °C and aged under N₂O/NO at 250 °C (○); pre-reduced at 250 °C and aged under N₂O/NO at 500 °C (◆); pre-reduced at 500 °C and aged under N₂O/NO at 400 °C (□); (a) N₂O conversion, (b) O₂ concentration.

erence PdO/LaCoO₃ which highlight a significant beneficial effect towards the conversion of N₂O. More interesting is the lower value obtained after ageing in the reactant mixture at 500 °C on pre-reduced Pd/LaCoO₃ in pure H₂ at 250 °C which is consistent with the highest conversion observed on this catalyst.

Steady state experiments were performed on the most active catalysts obtained after successive reductive (H₂ reduction at 250 °C) and ageing thermal treatment, respectively, at 250 and 500 °C. The conversion of N₂O and the correlative O₂ production are reported in Fig. 15. As observed, stable conversions versus time on stream are observable. Similar catalytic features as those previously reported from temperature-programmed ex-

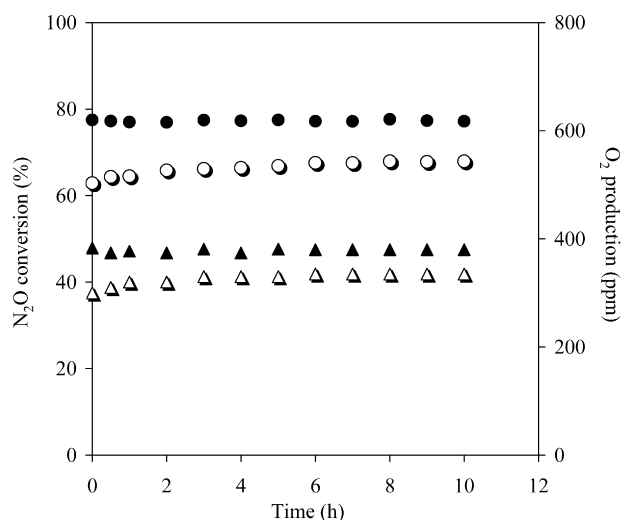


Fig. 15. Steady state catalytic measurements of pre-reduced and aged Pd/LaCoO₃ in the decomposition of N₂O in the presence of NO: N₂O conversion after pre-reduction at 250 °C and thermal ageing under N₂O/NO at 250 °C (○), pre-reduction at 250 °C and thermal ageing under N₂O/NO at 500 °C (●) O₂ production after pre-reduction at 250 °C and thermal ageing under N₂O/NO at 250 °C (△), pre-reduction at 250 °C and thermal ageing under N₂O/NO at 500 °C (▲).

periments emphasise the fact that the decomposition of N₂O predominantly takes place in both cases. Interestingly, a good agreement is obtained between temperature-programmed and steady state conversions recorded at 460 °C on the aged sample at 500 °C of, respectively, 0.74 and 0.77. Such a convergence agrees with the fact that both experiments characterise similar surface properties. On the other hand, some divergences arise by examining temperature-programmed and steady state measurements with a higher conversion on the aged sample at 250 °C obtained in this later case (0.67 against 0.48 from TP experiments). Such an increase in activity probably reflects additional surface modifications activated at 460 °C. In those temperature conditions a more extensive re-dispersion and the stabilisation of oxidic palladium species may originate this extra conversion.

3.2.3. Comparative study of freshly-prepared and aged catalysts in the decomposition of N₂O

The conversion profile vs temperature recorded on the freshly-prepared Pd/LaCoO₃ earlier reported in Fig. 12 during

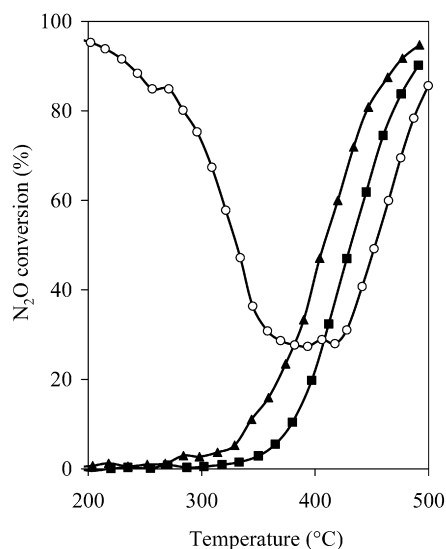


Fig. 16. Comparison of the catalytic activity of Pd/LaCoO₃ submitted to different activation treatments before temperature-programmed reaction: conversion of N₂O in the absence of NO on pre-reduced catalyst at 250 °C (○), conversion of N₂O in the absence of NO on the pre-reduced catalyst at 250 °C and aged under N₂O/NO at 500 °C (▲), conversion of N₂O with the presence of NO on the pre-reduced catalyst at 250 °C and aged under N₂O/NO at 500 °C (■).

the decomposition of N₂O in the absence of NO is compared with those obtained on aged catalysts in the presence and in the absence of NO, initially pre-reduced at 250 °C and exposed overnight to the reactive mixture at 500 °C (see Fig. 16). Clearly higher activities in the conversion of N₂O are observable on the aged catalyst irrespective of the feed gas composition, the light-off temperature shifting from 452 to 405 °C in the absence of NO and being intermediate ($T_{50} = 432$ °C) in the presence of NO. It is also noticeable that no NO conversion related to the formation of nitrites and/or nitrates significantly occurs on aged catalyst in comparison with reference PdO/LaCoO₃ in Fig. 13. Such a result agrees with previous observations related to the inhibiting effect of NO on the rate of N₂O conversion earlier evidenced on PdO/LaCoO₃. Probably, this detrimental effect is attenuated after successive reduction and ageing respectively at 250 and 500 °C due to significant redistribution of PdO clusters in strong interaction with the reconstructed perovskite. On the other hand it could be strengthened after pre-reduction at 500 °C because no surface reconstruction of the perovskite is observed after ageing. Such statements are in relative good agreement with the accumulation of nitrites and nitrates on this latter catalyst from XPS observations (see Fig. 9).

4. Discussion

The catalytic performances of Pd/Al₂O₃ and Pd/LaCoO₃ in the decomposition of N₂O in the presence or in the absence of NO strongly differ. Clearly, freshly-prepared Pd-modified perovskite catalysts exhibit higher overall activity in the conversion of N₂O in spite of their lower metal dispersion (0.16 against 0.86 on Pd/Al₂O₃). As a matter of fact, such a difference is not controversial but simply underlines the significant effect of the metal/support interaction on the catalytic performance

of supported palladium catalysts in the decomposition of N₂O. Such an extent of interaction may improve the Pd dispersion but also the intrinsic adsorption properties of palladium sites. These interpretations are supported by kinetic data reported in Table 3 which show significant changes on the apparent activation energy and on the estimates of the intrinsic rate according to the nature of the support. As indicated there is a good agreement between higher intrinsic rates and lower apparent activation energies on palladium supported on perovskite.

Coming back to the influence of the nature of the pre-activation thermal treatment on the overall activity in the decomposition of N₂O, only weak variations in the conversion, intrinsic rate and apparent activation energy values are discernible on PdO/Al₂O₃ and pre-reduced Pd/Al₂O₃ which suggest that both catalysts exhibit similar surface properties at high temperature. Such a tendency could be related to an extensive accumulation of oxygen atoms from the dissociation of NO and/or N₂O at the surface and/or a subsequent surface oxidation of metallic Pd particles during exposure under reactive conditions at high temperature. Consequently, oxidic palladium species as PdO_x would be probably involved in the reaction irrespective of the nature of the pre-activation thermal treatment. As previously mentioned, the lower apparent activation energies observed when PdO interacts with LaCoO₃ than those calculated on alumina indicate significant modifications of the reactivity of chemisorbed N₂O molecules towards the dissociation and/or the adsorptive properties of oxidic palladium species in interaction with LaCoO₃. Such arguments are in qualitative agreement with XPS measurements which indicate a significant shift of the Pd 3d_{5/2} core level towards higher BE values on the reference PdO/LaCoO₃ catalyst (336.8 eV against 336.1–336.4 eV on bulk and supported PdO on alumina [18]). Such observations could be associated to different chemical environments of Pdⁿ⁺ species on alumina and perovskite after calcination in air at 400 °C with correlative changes in the adsorptive properties of those oxidic Pd species. As a matter of fact, such changes in electronic properties of palladium entities may also reflect the creation of new active sites at the metal/support interface involving Pd²⁺ species and nearest neighbour anionic vacancies which could be potentially active in the decomposition of N₂O. There is no direct evidence of those active sites but H₂ temperature-programmed experiment provide additional observations which underline a significant effect of palladium on the reduction of Co³⁺ into Co²⁺. Based on this observation, palladium species could increase the reactivity of oxygen species from the perovskite. In the absence of reducing agent, their desorption could be assisted by the presence of palladium at high temperature with a subsequent formation of anionic vacancies. Such an explanation seems to be in rather good agreement with previous investigation of the CO + O₂ reaction on Pt/CeO₂ [26,27]. Those authors proposed two interpretations for explaining the effect of platinum on the reducibility of ceria by CO: (i) A weakening of the Pt–CO bond when platinum interact with reduced ceria. (ii) A charge transfer from metal to ceria accompanied with a small increase in the oxidation state of the metal and a decrease of the Ce–O bond strength correlatively [28]. Both considerations seem to be in good agreement

with the tendencies observed on the apparent activation energies for the decomposition of N_2O and on the binding energy level of the Pd 3d core level on freshly-prepared $\text{PdO}/\text{Al}_2\text{O}_3$ and $\text{PdO}/\text{LaCoO}_3$. The lower apparent activation energy and the higher intrinsic rate on $\text{PdO}/\text{LaCoO}_3$ than on $\text{PdO}/\text{Al}_2\text{O}_3$ can be connected to an unexpectedly high value for the binding energy of the Pd 3d core level in comparison with those currently reported for PdO on alumina. Such observations may reflect a charge transfer from Pd to LaCoO_3 leading to a small increase in the oxidation state of Pd and a decrease in the Co–O bond strength. Such correlations between kinetic and spectroscopic features suggest a greater ability to generate anionic vacancies via the destabilisation of Co–O bond at the vicinity of Pd species at high temperature.

Let us now examine the aged catalysts initially pre-reduced in pure H_2 then re-oxidised overnight under reaction mixture at high temperature. As previously shown, different catalytic behaviour has been reported according to the temperature of the pre-activation treatment in H_2 . It was found that successive pre-activation in H_2 at 250°C and re-oxidation in reactive conditions at 500°C promote the catalytic performances which exceed those recorded on a reference $\text{PdO}/\text{LaCoO}_3$. On the other hand, a pre-reduction at 500°C has no significant effect, the catalytic activity being comparable to that obtained on the reference $\text{PdO}/\text{LaCoO}_3$ catalyst. As observed the re-oxidation under reactive conditions of a pre-reduced catalyst at 500°C does not lead to the restoration of the perovskite structure but essentially to the segregation of La_2O_3 and Co_3O_4 contrarily to pre-activation thermal treatment at 250°C . The comparison of the atomic Pd/La ratio and metal dispersion also indicates a poorer palladium distribution probably due to thermal sintering in the course of the reduction at 500°C (see Table 2). More interesting is the examination of the apparent activation energy calculated on Pd/LaCoO₃ Red. 250°C –Ox. 500°C and the BE of Pd 3d. In fact the previous correlation established between both kinetic and spectroscopic features is accentuated with a lower apparent activation energy (42 kJ mol^{-1} against 55 kJ mol^{-1} on $\text{PdO}/\text{LaCoO}_3$) and a higher binding energy for Pd shifting from 336.8 to 337.2 eV. Consequently, the highest overall activity of Pd/LaCoO₃ Red. 250°C –Ox. 500°C is consistent with a redispersion of less reducible palladium species stabilised under unusual oxidation state in comparison between current BE values reported on reference PdO and PdO₂ samples. The reconstruction of the perovskite structure during thermal ageing could be the driving force in determining the extent of Pd dispersion with a partial incorporation of palladium inside the structure of the perovskite. Such a configuration would enhance the weakening of the Co–O bond with related formation of anionic vacancies for the dissociation of N_2O and explain the rate enhancement in the conversion of N_2O . As observed pre-reduction at 500°C has a detrimental effect on structural and catalytic properties due probably to thermal sintering which would inhibit the reconstruction of the perovskite and related re-dispersion of Pd species stabilised by the perovskite structure. In such conditions, oxygen-inhibiting effect could affect more extensively the rate of N_2O decomposition. Oxygen accumulation at the surface would enhance the formation of stable

nitrites and nitrates species which could also contribute in the loss of N_2O conversion.

5. Conclusion

This study reports the influence of successive reductive and oxidative pre-activation thermal treatments of supported Pd catalysts in the decomposition of N_2O in the absence and in the presence of NO. A higher activity of palladium sites is observed on LaCoO_3 than on Al_2O_3 which is not only related to the number of accessible Pd sites but also to the extent of interaction between oxidic palladium species and the support. It was found that the overall activity strongly depends on the nature of interactions between palladium species and the support generated during those successive thermal treatments. A high activity is obtained on $\text{PdO}/\text{LaCoO}_3$ after reduction in H_2 in smooth conditions at 250°C and re-oxidation after exposure to NO and N_2O at 500°C due to the re-dispersion of palladium species exhibiting an unusual oxidation state. On the contrary, a higher reduction temperature has a detrimental effect with the disappearance of the structure of the perovskite and probably the growth of palladium particles which affect the extent of the metal/support interface probably involved in the catalytic performances. It can be concluded that Pd and the perovskite have a cooperative effect on the overall activity in the decomposition of N_2O due to the creation of new active sites at the metal/support interface.

Acknowledgments

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References

- [1] M.A. Peña, J.L. Fierro, *Chem. Rev.* 101 (2001) 1981.
- [2] M. Sadakane, T. Asanuma, J. Kubo, W. Ueda, *Chem. Mater.* 17 (2005) 3546.
- [3] S. Kaliaguine, A. Van Neste, US Patent 6,017,504 (2000).
- [4] C.N. Costa, V.N. Stathopoulos, V.C. Belessi, A.M. Efstathiou, *J. Catal.* 197 (2001) 350.
- [5] C.N. Costa, P.G. Savva, C. Andronikou, P.S. Lambrou, K. Polychronopoulou, V.C. Belessi, V.N. Stathopoulos, P.J. Pomonis, A.M. Efstathiou, *J. Catal.* 209 (2002) 456.
- [6] M. Uenishi, M. Tanigushi, H. Tanaka, M. Kimura, Y. Nishihata, J. Mizuki, T. Kobayashi, *Appl. Catal. B* 57 (2005) 267–273.
- [7] F. Kapteijn, J. Rodrigues-Mirasol, J.A. Moulijn, *Appl. Catal. B* 9 (1996) 25.
- [8] G. Centi, L. Dall'Olio, S. Perathoner, *J. Catal.* 192 (2000) 224.
- [9] G. Centi, L. Dall'Olio, S. Perathoner, *J. Catal.* 194 (2000) 130.
- [10] V. Boissel, S. Tahir, C.A. Koh, *Appl. Catal. B* 64 (2006) 234.
- [11] A. Bueno-López, I. Such-Basáñez, C. Salinas-Martínez de Lecea, *J. Catal.* 144 (2006) 102.
- [12] J. Soria, A. Martínez-Arias, J.M. Coronado, J.C. Conesa, *Appl. Surf. Sci.* 70–71 (1993) 245.

- [13] H. Taguchi, S.I. Matsu-ura, M. Nagao, T. Choso, K. Kabata, J. Solid State Chem. 129 (1997) 60.
- [14] M. Engelmann-Pirez, P. Granger, L. Leclercq, G. Leclercq, Top. Catal. 30/31 (2004) 59.
- [15] R. Di Monte, P. Fornasiero, J. Káspár, A. Ferrero, G. Gubitosa, M. Graziani, Stud. Surf. Sci. Catal. 116 (1998) 559.
- [16] J.M. Gatica, R.T. Baker, P. Fornasiero, S. Bernal, J. Kaspar, J. Phys. Chem. B 105 (2001) 1191.
- [17] C.N. Costa, A.M. Efstathiou, J. Phys. Chem. B 108 (2004) 2620.
- [18] D. Briggs, M.P. Seah, in: Practical Surface Analysis, vol. 1, second ed., Wiley, New York, 1983, p. 613.
- [19] K.S. Kim, A.F. Gossmann, N. Winograd, Anal. Chem. 46 (2) (1974) 197.
- [20] S. Kaliaguine, A. Van Neste, V. Szabo, J.E. Gallot, M. Bassir, R. Muzychuck, Appl. Catal. A 209 (2001) 345.
- [21] M.M. Natile, E. Ugel, C. Maccato, A. Glisenti, Appl. Catal. B 72 (2007) 351.
- [22] L.G. Tejuca, J.L.G. Fierro, J.M.D. Tascon, Adv. Catal. 36 (1989) 237.
- [23] J.A. Marcos, R.H. Buitrago, E.A. Lombardo, J. Catal. 105 (1987) 95.
- [24] I. Twagirashema, M. Engelmann-Pirez, M. Frere, L. Burylo, L. Gengembre, C. Dujardin, P. Granger, Catal. Today 119 (2007) 100.
- [25] J.M. Giraudon, A. Elhachimi, F. Wyrwalski, S. Sieffert, A. Aboukais, J.F. Lamonier, G. Leclercq, Appl. Catal. B 75 (2007) 157.
- [26] C. Serre, F. Garin, G. Belot, G. Maire, J. Catal. 141 (1993) 1.
- [27] C. Serre, F. Garin, G. Belot, G. Maire, J. Catal. 141 (1993) 9.
- [28] H.C. Yao, Appl. Surf. Sci. 19 (1984) 398.