Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 137 (2008) 390–396

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Catalytic decomposition of N_2O on supported Pd catalysts: Support and thermal ageing effects on the catalytic performances

J.P. Dacquin, C. Dujardin, P. Granger *

Université des Sciences et Technologies de Lille, Unité de Catalyse et de Chimie du Solide,
UMR CNRS 8181, Bâtiment C3, 59655 Villeneuve d'Ascq Cedex, France

Abstract

This study is devoted to the catalytic decomposition of N_2O over noble metal-based catalysts under lean conditions in the presence of O_2, NO and water. A particular attention has been paid toward the influence of the support and the thermal ageing-induced effects on the catalytic properties of palladium species. In those operating conditions, the deposition of palladium on reducible supports, such as $LaCoO_3$, leads to higher activity in comparison with conventional supports such as alumina. Surface reconstructions take place during thermal ageing under reactive conditions on pre-reduced perovskite-based catalysts which lead to a significant rate enhancement in the decomposition of N_2O. On the other hand, it was found that oxygen and water strongly inhibit the surface reconstructions associated with changes in the selectivity towards the production of NO_2.

Keywords: Greenhouse gas; Nitrous oxide; N_2O catalytic decomposition; Perovskite; Supported noble metal-based catalysts; Nitric acid plant

1. Introduction

N_2O usually originates environmental problems as greenhouse gas [1]. Actually, the regulation of N_2O emissions from industrial sources seems to be the most feasible in comparison with diffuse agricultural sources [2,3]. Nitric acid plants received a particular attention because N_2O is usually an undesirable by-product from the catalytic oxidation of ammonia into nitric oxide, particularly over aged platinum–rhodium gauzes [4]. Different strategies for N_2O abatement have been recently suggested [3]. Among those solutions, catalytic processes for the decomposition of N_2O into N_2 and oxygen are usually considered as an attractive way but usually suffer from poisoning effects at low temperature due to strong adsorptions of O_2 and water [5–7]. Supported rhodium-based catalysts usually exhibit a high activity [5,6,8]. It was found that the stabilisation of well-dispersed cationic rhodium species on ceria surface promotes the overall activity [9]. Similar tendencies have been recently reported on supported Pd on perovskite [10]. It was found that redispersion processes of oxidic palladium species may take place according to the nature of the atmosphere during surface reconstructions of $LaCoO_3$. Those surface modifications originate a rate enhancement in the decomposition of N_2O. This study reports the effect of oxygen and water on those surface reconstructions during thermal ageing under reactive conditions and related changes on the catalytic performances.

2. Experimental

The preparation procedure of $LaCoO_3$ (20 $m^2\ g^{-1}$) using a so-called sol–gel method involving a citrate route was previously described [11,12]. $LaCoO_3$ and γ-Al_2O_3 (100 $m^2\ g^{-1}$) were impregnated by a palladium nitrate solution with adjusted concentrations in order to obtain 1 wt.% Pd. The precursor thus obtained was successively calcined in air at 400 °C and reduced in pure H_2 overnight at 250 °C. The calcined catalysts were labelled PdLaCo(C400) and PdAl(C400) and the reduced ones PdLaCo(R250) and PdAl(R250), respectively. H_2 chemisorption measurements performed at 100 °C for minimising the formation of bulk hydrides [10] led to Pd dispersion of approximately 0.86 and 0.16 according to an atomic H/Pd ratio equal to 1. The ageing procedure was performed overnight on PdLaCo(R250) and PdAl(R250) in isothermal conditions at 500 °C under reactive

---

* Corresponding author. Tel.: +33 3 20 43 49 38; fax: +33 3 20 43 65 61.
E-mail address: pascal.granger@univ-lille1.fr (P. Granger).

0920-5861/$ – see front matter
doi:10.1016/j.cattod.2008.01.016

mixture (1000 ppm NO and 1000 ppm N_2O) in the presence (wet conditions) or in the absence (dry conditions) of 3 Vol.% O_2 and 0.5 Vol.% H_2O. The aged samples were labelled respectively PdLaCo(R250A500H_2O) and PdLaCo(R250A500).

Temperature-programmed reduction experiments (TPR) were performed in a Micromeritics Autochem II 2920 apparatus (5 Vol.% H_2/Ar, 10 °C/min). X-ray diffraction (XRD) patterns were recorded on a HUBER G-670 diffractometer equipped with a Cu Kα (λ = 0.154 nm) radiation. X-ray photoelectron spectroscopic measurements (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 of C 1s (285.1 eV) as internal reference.

Temperature-programmed experiments were performed in a fixed-bed flow reactor using 0.7 g of catalyst in powder form with an average grain size of 80 μm with a gradual increase in temperature of 3 °C/min. The total flow rate was 15 L h^{-1}. H_2O was introduced into the reactor via a syringe. The effluents were analysed with a μGC VARIAN 4900 chromatograph fitted with two thermal conductivity detectors for the quantification of NO, O_2, N_2O and N_2 and a Balzer quadrupole mass spectrometer which allowed the detection of NO_2.

3. Results

3.1. Bulk and surface modifications of supported palladium catalysts after ageing

H_2 consumption profiles recorded on $LaCoO_3$ in the presence and in the absence of palladium are reported in Fig. 1. As observed a two-step reduction process earlier described [10] takes place with the occurrence of two distinct consumption ranges between 300 and 450 °C and between 500 and 650 °C. The bulk atomic H/Co ratio of respectively 1.04 ± 0.05 and 1.96 ± 0.09 on $LaCoO_3$ indicates the intermediate formation of Co(II) species. Clearly Pd incorporation induces a shift of the H_2 consumption profile toward lower temperatures which emphasizes the fact that Pd promotes the reduction of $LaCoO_3$. Additional bulk and surface characterisations were achieved on PdLaCo(C400) and PdLaCo(R250). XRD measurements did not reveal the segregation of La_2CoO_4, CoO_x (with $x = 1$ or 0) and La_2O_3 on PdLaCo(R250) due to an extensive bulk reduction (result not shown). XPS measurements performed on PdLaCo(C400), PdLaCo(R250) show significant surface changes according to reductive and oxidative thermal treatments. As illustrated in Fig. 2A, Co 2p1/2 and Co 2p3/2 spectra recorded on PdLaCo(C400) are located, respectively at 795.1 and 779.9 eV accompanied with a shake-up structure at 789.5 eV which characterises the predominance of Co(III) species stabilised at the surface inside the structure of $LaCoO_3$. This shake-up structure appears at lower binding energy values (785.6 eV) on PdLaCo(R250) which underlines an extensive surface reduction of Co(III) into Co(II). Parallel to these changes, a significant shift of the B.E. value of Pd 3d5/2 core level is distinguishable from 336.8 to 335.4 eV, which shows the reduction of Pd(II) into metallic Pd particles (see Fig. 2B). Parallel to these observations no significant change occurs on the surface atomic Pd/La ratio calculated on PdLaCo(C400) and PdLaCo(R250) (see Table 1). Subsequent investigations on aged PdLaCo(R250A500) and PdLaCo(R250A500H_2O), respectively under dry and wet atmospheres reveal additional surface modifications. As observed in Fig. 2A, the disappearance of the shake-up structure characteristic of Co(II) species in the Co 2p photopeak reveals an extensive surface re-oxidation of Co(II) into Co(III) species both on PdLaCo(R250A500) and PdLaCo(R250A500H_2O). Interestingly, the Pd 3d5/2 core level shifts towards higher B.E. values on PdLaCo(R250A500) (337.2 versus 336.8 eV on PdLaCo(C400)). Correlatively a significant increase in the relative intensity of the Pd 3d photopeak is observable. Different spectral features characterise PdLaCo(R250A500H_2O) with relative intensity of the photopeak Pd 3d substantially lower than that obtained on PdLaCo(R250A500). Such changes are summarised in Table 1. As indicated, the broadening observed on the Pd 3d photopeak recorded on PdLaCo(R250A500H_2O) is probably related to the segregation of oxidic Pd(II) species in various chemical environments. Those XPS results indicate that the redispersion evidenced on PdLaCo(R250A500) during ageing under dry atmosphere is strongly inhibited under wet atmosphere in the presence of H_2O and O_2. An additional ageing process in 5% O_2/He was performed on PdLaCo(R250) (in the absence of NO, N_2O and water). Spectral features of PdLaCo(R250O500), summarised in Table 1, are comparable with those previously obtained on PdLaCo(R250A500H_2O) with binding energy values and relative surface Pd composition varying within the margin of error.

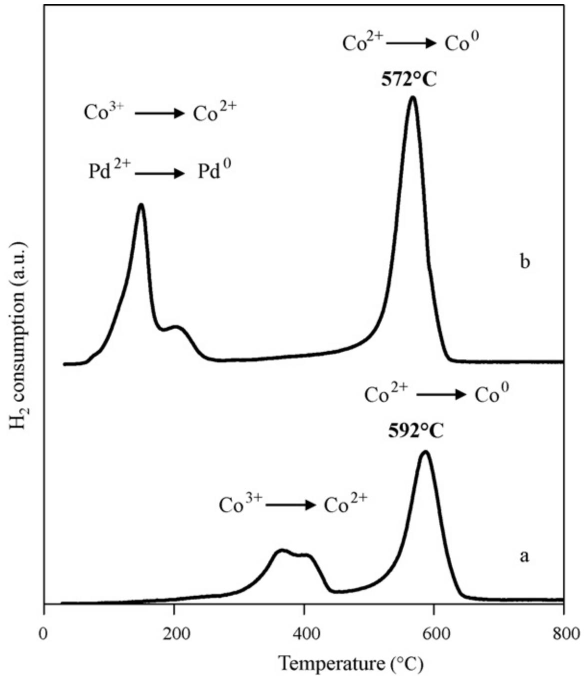

Fig. 1. Temperature-programmed reduction under 5% H_2/Ar on $LaCoO_3$ (a) and on PdLaCo(C400) (b).

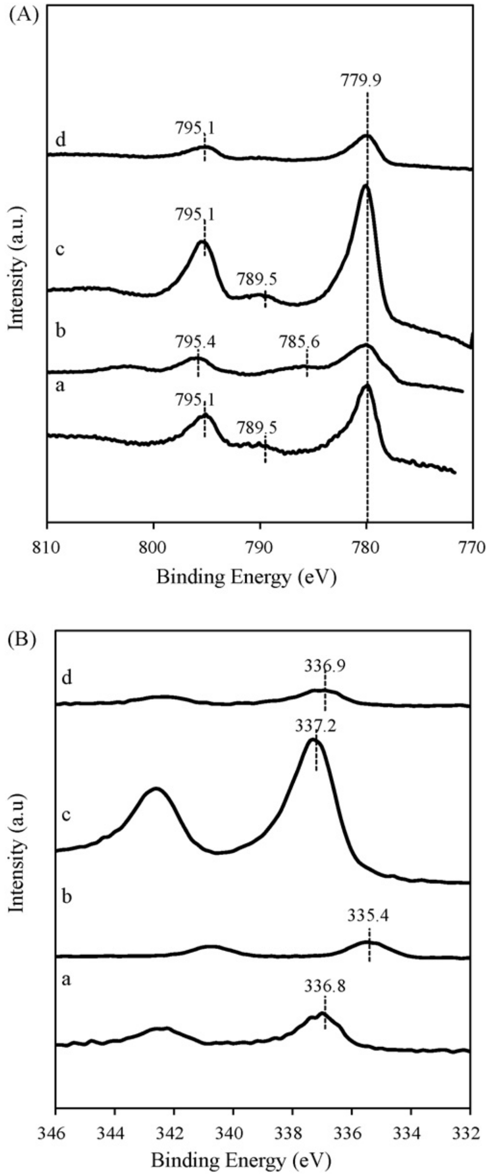

Fig. 2. Surface analysis by X-ray photoelectron spectroscopy: Co 2p spectra (A) and Pd 3d spectra (B) recorded on PdLaCo(C400) (a), PdLaCo(R250) (b), PdLaCo(Red250A500) (c) and PdLaCo(Red250A500H_2O) (d).

3.2. Catalytic performances in the decomposition of N_2O on supported Pd catalysts

3.2.1. On alumina

The decomposition of N_2O in the presence of NO under dry atmosphere has been investigated on PdAl(C400) and PdAl(R250). In this first attempt, we have examined the catalytic performances of respectively oxidic and metallic palladium species interacting with alumina. In the temperature range of the study, no significant NO conversion was detected (NO conv. $< 2.5\%$). As observed in Fig. 3, the conversion of N_2O on PdAl(C400) becomes significant above 400 °C reaching 45% at 500 °C. PdAl(R250) exhibits a lower N_2O conversion (25%) at that temperature. The apparent activation energy calculated from temperature-programmed conversions and the specific rate estimated at 460 °C are collected in Table 2. The intrinsic rates have been calculated from the number of accessible Pd atoms obtained from H_2 titration. As indicated in Table 2, PdAl(C400) and PdAl(R250) exhibit comparable values for E_{app} according to the margin of error. Now, regarding the catalytic performances of PtAl(R250A500H_2O) under wet atmosphere, in the presence of 1000 ppm NO, 1000 ppm N_2O, 3 Vol.% O_2 and 0.5 Vol.% H_2O, a different catalytic behaviour is noticeable associated with an extra O_2 consumption assigned to the formation of NO_2 (see Fig. 3b). On the other hand, an extra O_2 formation associated with the catalytic decomposition of N_2O starts above 450 °C.

3.2.2. On perovskite $LaCoO_3$

Fig. 4 shows N_2O conversion profiles recorded under dry atmosphere on PdLaCo(C400) and PdLaCo(R250). The correlative production of oxygen is also reported. As previously observed on supported alumina catalysts no significant NO conversion takes place. It is worthwhile to note that PdLaCo(C400) exhibits a higher overall activity in the conversion of N_2O than PdAl(C400) (see Fig. 3) in spite of its lower metal dispersion. Such an observation can partly be explained by the intrinsic activity of $LaCoO_3$ towards N_2O reported elsewhere [10]. Alternately, changes in the extent of interaction with the support might also be considered and could modify the adsorptive properties of Pd species. We have tentatively calculated the intrinsic rate and the apparent

Table 1
XPS measurements of 1 wt.% Pd/$LaCoO_3$ catalysts after various thermal treatments in controlled atmospheres

Catalyst	Thermal ageing	B.E.[a] Pd $3d_{5/2}$ (eV)	Peak width[b] (eV)	Surface Pd composition[c]
PdLaCo(C400)	Calcined at 400 °C in air	336.8 ± 0.2	1.6	0.04
PdLaCo(R250)	Reduced at 250 °C in H_2	335.4 ± 0.2	1.6	0.035
PdLaCo(R250A500)	Reduced at 250 °C and aged under N_2O/NO at 500 °C	337.2 ± 0.2	1.6	0.11
PdLaCo(R250A500H_2O)	Reduced at 250 °C and aged under N_2O/NO/O_2/H_2O at 500 °C	336.9 ± 0.2	2	0.035
PdLaCo(R250O500)	Reduced at 250 °C and aged under 5% O_2/He at 500 °C	337.0 ± 0.2	2	0.045

[a] Binding energy.
[b] Full width at half maximum of the Pd $3d_{5/2}$ photopeak.
[c] Atomic Pd/La ratio from XPS experiments, relative accuracy equal to ±20%.

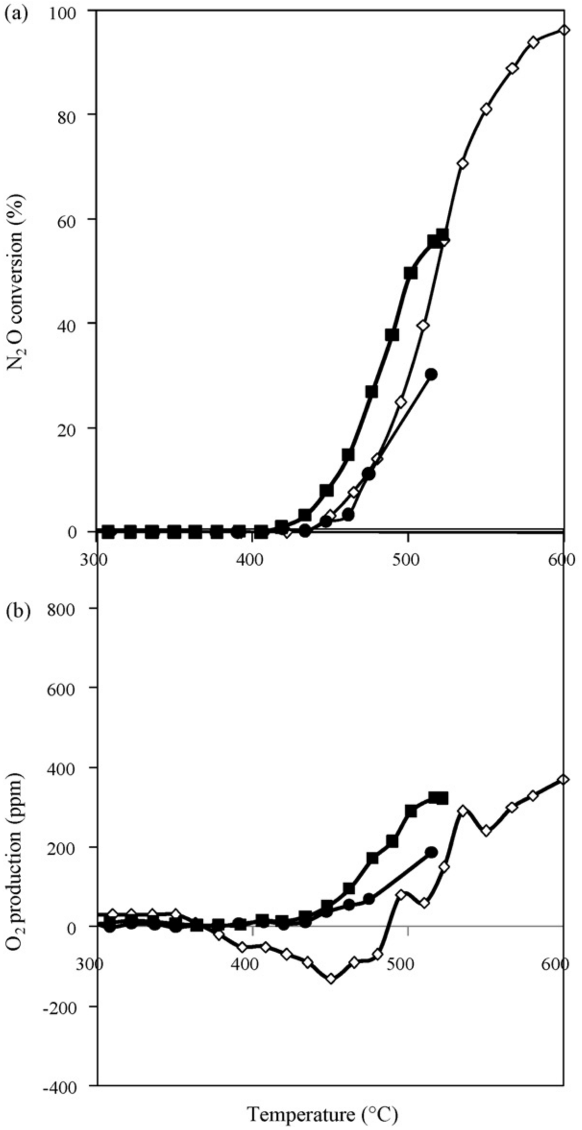

Fig. 3. Temperature-programmed experiments for the decomposition of N_2O on Pd/Al_2O_3 under dry atmosphere in the presence of 1000 ppm N_2O and 1000 ppm NO (full symbols) and wet atmosphere in the presence of 1000 ppm N_2O, 1000 ppm NO, 3 Vol.% O_2 and 0.5 Vol.% H_2O (open symbols). N_2O conversion (a) and O_2 production (b) on PdAl(C400) (■), PdAl(R250) (●), and PdAl(R250A500H_2O) (◇).

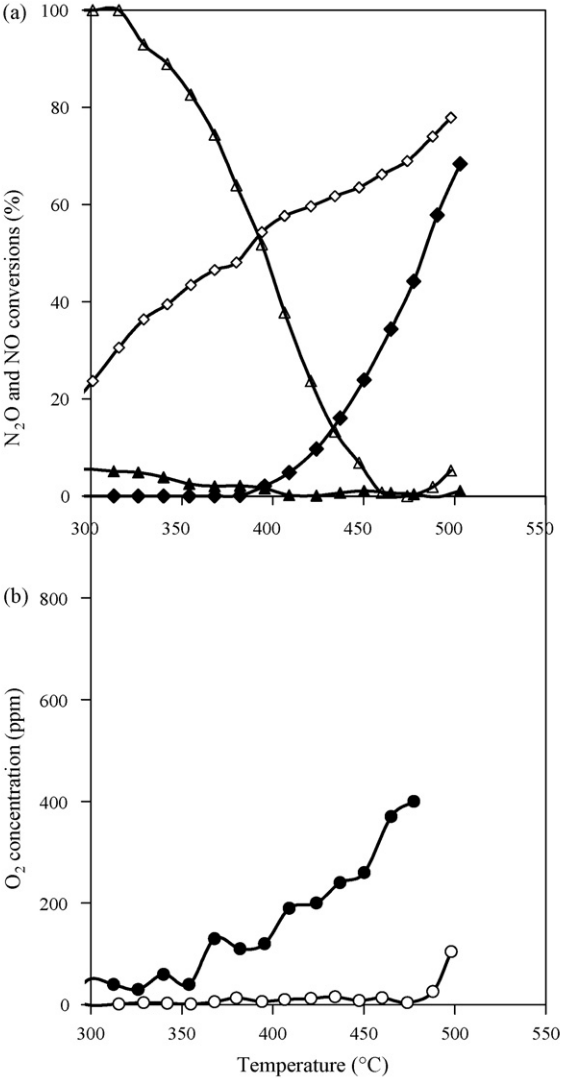

Fig. 4. Temperature-programmed experiments for the decomposition of N_2O on PdLaCo(C400) and PdLaCo(R250) in the presence of 1000 ppm N_2O, 1000 ppm NO diluted in He: N_2O conversion (◆), NO conversion (▲) (a) and O_2 concentration (●) (b) on PdLaCo(C400); N_2O conversion (◇), NO conversion (△) (a) and O_2 concentration (○) (b) on PdLaCo(R250).

activation energy based on the same above-mentioned procedure described on Pd supported on alumina. The estimates are reported in Table 3. As observed, higher intrinsic rate and lower E_{app} characterise PdLaCo(C400) in comparison with

Table 2
Catalytic performances of supported Pd on alumina in the decomposition of N_2O

Catalyst	Thermal ageing	N_2O conversion (%)[a]	Specific rate[a] (mol h^{-1} g^{-1})	Intrinsic rate[b] (mol h^{-1} Pd_{surf}^{-1})	Apparent activation energy (kJ mol^{-1})
PdAl(R250)[c]	Reduced at 250 °C	4	3.5×10^{-5}	0.4[c]	89 ± 5
PdAl(C400)[c]	Calcined at 400 °C	15	1.3×10^{-4}	1.6[c]	93 ± 5
PdAl(R250A500H_2O)[d]	Reduced at 250 °C and aged under $N_2O/NO/O_2/H_2O$ at 500 °C	6	5.3×10^{-5}	0.7	84 ± 3

[a] Calculated at 460 °C from TPR experiments.
[b] Based on the number of surface Pd atoms calculated from H_2 titration.
[c] Temperature-programmed experiment in the presence of 1000 ppm NO and 1000 ppm N_2O (dry atmosphere).
[d] Temperature-programmed experiment in the presence of 1000 ppm NO, 1000 ppm N_2O, 3 Vol.%O_2 and 0.5 Vol.%H_2O (wet atmosphere).

Table 3
Catalytic performances of supported Pd on $LaCoO_3$ in the decomposition of N_2O

Catalyst	Thermal ageing	N_2O conv. (%)[a]	Specific rate[a] (mol h^{-1} g^{-1})	Intrinsic rate[b] (mol h^{-1} Pd_{surf}^{-1})	Apparent activation energy (kJ mol^{-1})
PdLaCo(C400)[c]	Calcined at 400 °C	32	2.8×10^{-4}	19	55 ± 3
PdLaCo(C400)[d]	Calcined at 400 °C	10	0.9×10^{-4}	6	50 ± 3
PdLaCo(R250A500)[c,e]	Reduced at 250 °C and aged under N_2O/NO at 500 °C	74	6.5×10^{-4}	66	42 ± 3
PdLaCo(R250A500H_2O)[d]	Reduced at 250 °C and aged under $N_2O/NO/O_2/H_2O$ at 500 °C	16	1.4×10^{-4}	9	54 ± 3

[a] Calculated at 460 °C from TPR experiments.

[b] Based on the number of surface Pd atoms calculated from H_2 titration.

[c] Temperature-programmed experiment in the presence of 1000 ppm NO and 1000 ppm N_2O (dry atmosphere).

[d] Temperature-programmed experiment in the presence of 1000 ppm NO, 1000 ppm N_2O, 3 Vol.%O_2 and 0.5 Vol.%H_2O (wet atmosphere).

[e] See Ref. [10].

PdAl(C400) (55 kJ mol^{-1} versus 93 kJ mol^{-1}). More complex catalytic features are observable on PdLaCo(R250) associated with a complete NO conversion starting below 300 °C without simultaneous production of oxygen in the gas phase. A decrease in NO conversion starts above 300 °C parallel to an increase in N_2O conversion but still without significant production of O_2 which indicates a predominant re-oxidation of the solid. In fact, O_2 production becomes distinguishable above 450 °C. In that temperature range, the re-oxidation of the solid is complete and the catalytic decomposition on re-oxidized catalyst is activated with the correlative formation of nitrogen and oxygen in the gas phase. It is worthwhile to note that the extent of N_2O decomposition is lower on PdLaCo(R250) than on PdAl(R250) based on the comparison of O_2 concentration curves.

Thermal ageing processes under reactive conditions in dry or wet atmosphere have been implemented in order to obtain a complete bulk and surface re-oxidation and then investigate the catalytic decomposition without any interference. However, XPS investigations, respectively on PdLaCo(R250A500) and PdLaCo(R250A500H_2O), revealed significant surface changes associated with a partial redispersion of oxidic palladium species particularly on PdLaCo(R250A500) (see Fig. 2) while this phenomenon seems to be inhibited on PdLaCo(R250A500H_2O). Temperature-programmed conversion curves recorded on aged Pd/$LaCoO_3$ under dry or wet atmosphere are compared in Fig. 5a. The simultaneous production of oxygen produced from the decomposition of N_2O has also been reported in Fig. 5b. As illustrated, only the catalytic decomposition of N_2O takes place on PdLaCo(R250A500) with no extra O_2 consumption assigned to bulk and surface re-oxidation and/or NO oxidation to NO_2 during TPR experiments. It is remarkable that PdLaCo(R250A500) exhibits a higher activity than PdLaCo(C400). Such a comparison has been already discussed and highlights the beneficial effect of the thermal ageing under dry conditions on the catalytic performances in the decomposition of N_2O [10]. Such a beneficial effect is accompanied by a decrease in the apparent activation energy (42 kJ mol^{-1} versus 55 kJ mol^{-1} on PdLaCo(C400) see Table 3). Now, regarding the influence of thermal ageing in the presence of O_2 and water, the surface properties are differently affected with a significant change in the catalytic behaviour of PdLaCo(R250A500H_2O). Clearly, an extra O_2 consumption occurs in the low temperature range which corresponds to the formation of NO_2. The NO conversion into NO_2 stops above 450 °C. In that temperature range the decomposition of N_2O predominates. As seen in Fig. 5, the conversion of N_2O at 500 °C drops from 74% on PdLaCo(R250A500) under dry conditions to 16% on PdLaCo(R250-

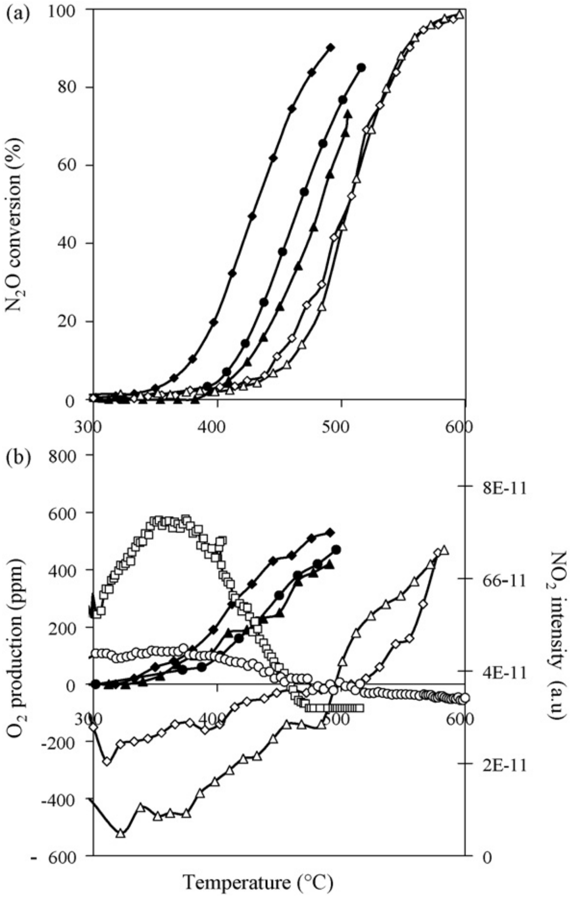

Fig. 5. Temperature-programmed experiments for the decomposition of N_2O on Pd/$LaCoO_3$ under dry atmosphere in the presence of N_2O and NO (full symbols) and wet atmosphere in the presence of N_2O, NO, O_2 and H_2O (open symbols). N_2O conversion (a), O_2 production (b) on PdLaCo(R250A500) (◆), PdLaCo(R250A500O_2) (●), PdLaCo(C400) (▲), PdLaCo(R250A500H_2O) (◇) and PdLaCo(C400) (△) catalysts, and NO_2 production (b) on PdLaCo(R250A500H_2O) (○) and PdLaCo(C400) (□).

A500H_2O) under wet conditions. Such a loss of activity is well in agreement with a subsequent increase in the apparent activation energy on PdLaCo(R250A500H_2O) (54 kJ mol^{-1} versus 44 kJ mol^{-1}) becoming comparable with that obtained on PdLaCo(C400).

TPR experiments in wet atmosphere were also performed on PdLaCo(C400) for further comparisons. As observed in Fig. 5, the N_2O conversion curve is superposed to that previously recorded on PdLaCo(R250A500H_2O). Moreover, PdLaCo(C400) behaves similarly at low temperature with a significant NO_2 formation. However, it seems obvious that the production of NO_2 occurs in lesser importance on PdLaCo(R250A500H_2O) than on PdLaCo(400) which is still in agreement with a beneficial effect of the thermal ageing.

4. Discussion

Results reported in this investigation clearly reveal a significant effect of the nature of the support on the overall activity of supported palladium catalysts on alumina and on perovskite ($LaCoO_3$). As observed lower intrinsic activities and higher apparent activation energies characterise PdAl(C400) and PdAl(R250). In our operating conditions, oxidic palladium species on alumina are likely involved in the decomposition of N_2O. On the other hand, different catalytic performances characterise PdLaCo(C400) because Pd and $LaCoO_3$ are active in the decomposition of N_2O according to previous observations [10]. Consequently, the definition of the active sites seems to be more complex on Pd/$LaCoO_3$ than on Pd/Al_2O_3 because oxidic Pd species and $LaCoO_3$ should cooperate with the occurrence of synergistic effects. Such a feature is usual when noble metals interact with reducible supports such as CeO_2 [14]. Generally, the rate enhancement is often related to the redox properties of the support with the presence of labile oxygen species. Additional parameters have to be accounted for related to the local environment of Pd entities which may change according to the degree of dispersion and the extent of interaction of Pd entities with $LaCoO_3$. Such changes may explain the different catalytic behaviour of PdLaCo(R250A500) and PdLaCo(R250A500H_2O). Such an interaction can be discussed on the basis of H_2 temperature-programmed reduction experiments and mainly XPS observations. Binding energy values of the Pd 3d photopeak recorded on PdLaCo(C400) characterise Pd^{2+} species probably stabilised as PdO. However, it is noteworthy that the value of 336.8 eV is slightly higher than those currently reported on bulk and supported PdO on alumina [13] in the range 336.1–336.4 eV. Previous experiments on oxidised 1 wt.% Pd/Al_2O_3 performed in our laboratory led to a value of 336.3 eV in agreement with the literature data [14]. Such observations may suggest different extent of interaction between Pd^{2+} entities dispersed on alumina and on $LaCoO_3$. Accordingly, their adsorptive properties and the reactivity of chemisorbed N_2O molecules toward the dissociation may change in agreement with lower apparent activation energies and higher intrinsic rates on PdLaCo(C400) than on PdAl(C400). The reactivity of oxygen species from $LaCoO_3$ may also depend on the extent of interaction with Pd species. This is well illustrated from H_2 temperature-programmed reduction experiments in Fig. 1 which evidence a significant beneficial effect of palladium incorporation on the reduction of Co(III) into Co(II). At relatively high temperature, the presence of palladium species could activate the partial desorption of labile oxygen species from $LaCoO_3$ with a subsequent formation of anionic vacancies potentially active for the dissociation of chemisorbed N_2O. Such an assumption can be discussed in the light of previous investigations dealing with the $CO + O_2$ reaction of Pt deposited on ceria which also activate the reaction due to the presence of those labile oxygen species [15]. The authors proposed two interpretations for explaining the effect of ceria: (i) a weakening of the usual CO inhibiting effect; (ii) a charge transfer from Pt to ceria which leads to a small increase in the oxidation state of Pt and correlatively to a decrease of the Ce–O bond strength [16]. This latter interpretation seems to be in relative good agreement with changes observed on the B.E. values of Pd and on the apparent activation energies. The slight increase in the B.E. value of Pd 3d on PdLaCo(C400) with the correlative decrease in the apparent activation energy in comparison with PdAl(C400) could be associated to a greater ability to generate at high temperature anionic vacancies via the destabilisation of Co–O bond assisted by the presence of Pd. Such a tendency is more accentuated on PdLaCo(R250A500) which exhibits the highest activity in the decomposition of N_2O. As observed in Table 1, the shift in the B.E. value of Pd $3d_{5/2}$ core level to higher values can be correlated to a lowering in the apparent activation energy in comparison with PdLaCo(C400).

Now, the examination of catalytic performances under wet atmosphere on PdAl(R250A500H_2O) and PdLaCo(R250A500H_2O) leads to completely different catalytic performances with a significant loss of activity. Two aspects have to be considered for explaining this results: (i) structural modifications induced by the presence of oxygen and water during thermal ageing and (ii) inhibiting effects on the rate of N_2O decomposition due to strong adsorption of oxygen and water and/or the stabilisation of nitrate species [10] via the formation of NO_2 in the gas phase. As a matter of fact, XPS analysis did not reveal a significant accumulation of N-containing species at the surface of PdLaCo(R250A500H_2O) in comparison with PdLaCo(R250A500). Clearly, XPS measurements show a detrimental effect on the redispersion of oxidic palladium species after ageing under wet atmosphere. Pd 3d photopeak strongly attenuates and broadens on PdLaCo(R250A500H_2O) with an apparent maximum shifting towards lower binding energy values which suggests the segregation of oxidic Pd species in different chemical environments. Parallel to this observation an increase in E_{app} is evidenced. Previous investigations dealt with surface reconstructions of noble metals during the decomposition of N_2O. By way of illustration Centi et al. [5,6] reported on Rh supported on zirconia surface reconstruction above a certain limit of oxygen coverage, such an effect being also dependent on the extent of interaction between Rh particles and the support which varies according to the presence or the absence of water. Boisel et al. [7] discussed on the detrimental effect of oxygen on the rate of N_2O decomposition. In fact, improvements of the resistance to oxygen inhibition could be related to a high dispersion of the active sites, O_2 would be more strongly adsorbed on large Pd and PdO clusters [7]. Clearly, oxygen and water favour thermal sintering process on PdLaCo(R250A500H_2O) according to XPS observations. Correlatively, a strengthening of O_2 and water inhibiting effects on the rate of N_2O decomposition is observed. In fact, the preferential formation of PdO at the expense of isolated Pd^{2+} and/or well-dispersed PdO clusters strongly interacting with $LaCoO_3$ would explain such inhibiting effects and also the occurrence of NO_2 formation. However, it is worthwhile to note that PdLaCo(R250A500H_2O) still preserves a higher activity in N_2O decomposition than PdAl(R250A500H_2O) and PdLaCo(C400) with a higher NO_2 production on this latter catalyst which emphasizes the fact that surface modifications previously evidenced on PdLaCo(R250A500) attenuate but still occur in the presence of O_2 and H_2O.

5. Conclusion

This study reports the influence of successive reductive and oxidative thermal treatments of supported Pd catalysts in the decomposition of N_2O in the absence and in the presence of an excess of O_2 and water. A higher activity is observed on $LaCoO_3$ than on Al_2O_3 which has not been related to the number of accessible Pd sites but mainly to the extent of interaction between oxidic palladium species and the support. Thermal ageing in dry conditions has a beneficial effect on the activity in N_2O decomposition assigned to a Pd redispersion on $LaCoO_3$. On the other hand, such a process is partly inhibited under wet atmosphere in the presence of O_2 and H_2O during the reaction with a significant loss of N_2O conversion and the parallel production of NO_2. Nevertheless, it was found that the NO_2 formation attenuates on the aged Pd/$LaCoO_3$ under wet conditions.

Acknowledgments

We thank the Institute of Research in Industrial Environment supported by Region Nord-Pas-de-Calais, and the Ademe for a grant (J.-P. Dacquin).

References

[1] L. Donner, V. Ramanathan, J. Atmos. Sci. 37 (1980) 119.

[2] F. Kapteijn, J. Rodriguez-Mirasol, J.A. Moulijn, Appl. Catal. B 9 (1996) 25.

[3] J. Pérez-Ramirez, F. Kapteijn, K. Schöffel, J.A. Moulijn, Appl. Catal. B 44 (2003) 117.

[4] J. Pérez-Ramirez, F. Kapteijn, G. Mul, X. Xu, J.A. Moulijn, Catal. Today 76 (2002) 325.

[5] G. Centi, L. Dall'Olio, S. Perathoner, J. Catal. 192 (2000) 224.

[6] G. Centi, L. Dall'Olio, S. Perathoner, J. Catal. 194 (2000) 130.

[7] V. Boissel, S. Tahir, C.A. Koh, Appl. Catal. B 64 (2006) 234.

[8] A. Bueno-López, I. Such-Basáñez, C. Salinas-Martínez de Lecea, J. Catal. 144 (2006) 102.

[9] J. Soria, A. Martinez-Arias, J.M. Coranado, J.C. Conesa, Appl. Surf. Sci. 70/71 (1993) 245.

[10] J.P. Dacquin, C. Dujardin, P. Granger, J. Catal. 253 (2008) 37.

[11] H. Taguchib, S.I. Matsu-urab, M. Nagaob, T. Choso, K. Tabata, J. Solid State Chem. 129 (1997) 60.

[12] M. Engelmann-Pirez, P. Granger, L. Leclercq, G. Leclercq, Top. Catal. 30/31 (2004) 59.

[13] D. Briggs, M.P. Seah, Second ed., Practical Surface Analysis, vol. 1, Wiley, New York, 1983, p. 613.

[14] A.-S. Mamede, G. Leclercq, E. Payen, P. Granger, L. Gengembre, J. Grimblot, Surf. Interface Sci. 34 (2002) 105.

[15] C. Serre, F. Garin, G. Belot, G. Maire, J. Catal. 141 (1993) 1;
C. Serre, F. Garin, G. Belot, G. Maire, J. Catal. 141 (1993) 9.

[16] H.C. Yao, Appl. Surf. Sci. 19 (1984) 398.