Submitted to the Journal of Catalysis

Catalytic after-treatment for NO and N_2O abatement from nitric acid plants : A sequential approach using noble metal modified perovskites

Y. Wu[1], C. Dujardin[1], C. Lancelot[1], J.P. Dacquin[1],
V. Parvulescu[2]*, M. Cabié[3,4], C.R. Henry[3], T. Neisius[4], P. Granger[1]*

[1] *Unité de Catalyse et de Chimie du Solide UMR 8181, Université Lille1 Sciences and Technologies, Cité scientifique, bâtiment C3, 59650 – Villeneuve d'Ascq, France*

[2] *University of Bucharest, Faculty of Chemistry, Department of Organic Chemistry, Biochemistry and Catalysis, 4 – 12 Regina Elisabeta Bvd., Bucharest 030016, Romania*

[3] *Centre Interdisciplinaire de Nanoscience de Marseille, CNRS UPR 3118, Associated to Aix-Marseille Université, Campus Luminy, 13288 Marseille, France*

[4] *Fédération des Sciences Chimiques de Marseille, Aix Marseille Université, 13397 Marseille Cedex 20, France*

---

* Corresponding authors : vasile.parvulescu@g.unibuc.ro
Tel./Fax number : +40 21 4100241

pascal.granger@univ-lille1.fr
Tel. number : +33 3 20 43 49 38
Fax number : + 33 3 20 43 65 61

Abstract

A combined study was achieved to remove sequentially trace amount of N_2O and NO from nitric acid plants. Catalytic systems involving perovskite-type materials have been developed in which precious metals were incorporated in order to compensate deactivation processes for high temperature N_2O decomposition and to enhance the usual low temperature activity in NO conversion. In both cases, specific interactions are needed to preserve the metal dispersion at high temperature and to generate cooperative effects at low temperature ascribed to the creation of active sites at the metal/support interface. It has been shown that the reducibility of the perovskite can be a key factor especially when sol-gel method is used to enhance the concentration of PdO_x nano-sized clusters in interaction with $LaCo_{1-x}Pd_xO_3$ through a partial extraction of palladium species initially localized inside the perovskite lattice via appropriate redox thermal treatments. An optimum has been observed when the initial catalyst was reduced and reoxidized in wet atmosphere which accelerate the reconstruction of the perovskite structure with Pd onto the support in stronger interaction corresponding to a high increase of the normalized rates. For NO removal at low temperature, Pt has been incorporated via a classical wet impregnation. A re-dispersion of the active phase occurs at the surface taking into account the weak reducibility of $LaFeO_3$. Moderate temperatures for oxidative/reductive thermal treatments leads to significant enhancement in NO conversion ascribed to the growth of epitaxially orientated Pt particles. When these thermal treatments proceed at high temperature (500°C instead of 300°C) a detrimental effect on the activity at low temperature is observed ascribed to a strong alteration of the metal/support interface as observed from HRTEM analysis.

Keywords : Catalytic N_2O decomposition, NO/H_2 reaction, Nitric acid nitric plant, Precious metals, Perovskite

1. Introduction

The emission of greenhouse gas is partly related to the development of industrialized countries since 150 years. More recently, the scientific community pointed out the relationship between anthropogenic emissions with climate changes. This led the European countries to sign the Kyoto Protocol [1] which committed themselves to reduce their emissions by at least 5% during the period 2008-2012 [2]. Particular attention was paid in the last two decades to anthropogenic N_2O emissions having a higher Global Warming Potential ~300 times higher than that of CO_2 and a longer lifetime [2]. First attempts concerned adipic acid plants with outlet gas containing high concentration of N_2O (30-50 vol.%) as primary side product [3,4]. Significant reduction was successfully obtained using catalytic systems running at medium temperature in the absence of significant amount of water in the exhaust gas [5]. For nitric acid plants the implementation of efficient N_2O abatement system is more challenging with the formation of significant lower amount of N_2O from incomplete ammonia oxidation in the course of the deactivation of Pt-Rh gauzes used as catalyst for ammonia oxidation. Different options have been previously classified [4] as primary, secondary and tertiary technologies. As illustrated in Fig. 1, primary solutions consist of modifying the oxidation process especially the design of Pt-Rh gauzes to improve their thermal stability. Secondary technologies are commercially available dedicated to the implementation of catalytic systems able to decompose N_2O at high temperature e.g. unsupported cobalt-oxide spinel structures with composition $Co_{3-x}M_xO_4$ (M = Fe, Al, Co and x = 0–0.2) have been reported [6]. Yttrium stabilized zirconia [7], ceria-zirconia [8] were also investigated at the lab-scale. According to this option, catalytic systems are installed inside the ammonia burner to convert N_2O immediately after its formation. Specific requirements are needed especially a high thermal stability with running temperature above 900°C in wet atmosphere and a good

Commenté [P1]: Introduire la référence Appl. Catal. B 44 (2003) 117-151
Avec un commentaire

selectivity to avoid loss of nitric acid yield through partial NO conversion. Finally, tertiary technologies aim to convert N_2O and NO simultaneously either upstream or downstream the tail gas expander and need more intrinsically active phases such as precious metals. Generally, the use of reducing agents is requisite especially for end-of-pipe technologies with low-temperature exhaust gas.

As a matter of fact, it has been already pointed out that the secondary technology is cost efficient but its practicability is intimately related to the stability of the catalyst. It was earlier demonstrated that perovskite type oxides can be profitably used for such an application. Previously, Porzellanwerk Kloster Veilsdor already patented supported $LaCoO_3$ perovskite as active phase for the decomposition of N_2O at high temperature [9]. Also, Umicore developed various compositions of perovskites [10]. The interest in the use of $LaCoO_3$ perovskite can be related to their behavior developing specific surface after steam treatment at atmospheric pressure up to 800°C as shown by Choudhary et al. [11]. However, at high temperature, significant surface reconstructions attributed to partial substitution of Co site by Pd [12] or iron can occur [13] with the segregation of Co_3O_4. Incorporation of Rh has been previously envisaged for moderate and high temperature applications [14,15] especially for the decomposition of N_2O propellant [16,17]. High running temperature leads inevitably to losses of activity mainly due to sintering. To compensate deactivation, platinum group metals (PGM), especially Rh which exhibits a much higher activity, can be added through conventional impregnation methods. However, the resulting material can also suffer from deactivation due to crystal transition and Rh volatilization [16]. Alternately, noble metals can be stabilized inside the perovskite structure or through reductive/oxidative pretreatments which can promote a greater stabilization of nano sized noble metal particles [16]. The concept of intelligent catalysts was earlier associated to the self-regenerative behavior of noble metal modified-perovskites under three-way conditions with dynamic processes which stabilize the metal dispersion contrarily to conventional catalysts supported on alumina where noble metals weakly interact and then irreversibly sinter [17-21]. Based on this concept various strategies were developed to stabilize at the surface nanostructures such as those reported on Pt/CeO_2 [22] with the formation of nano composite oxides that involve the formation of a Pt–O–Ce bond. Similarly, strong interactions can be obtained when noble metals are conventionally deposited on perovskite via impregnation rather than sol-gel methods adopting optimal redox treatments to promote such type of interactions. Those transformations have been essentially characterized on Pd/$LaCoO_3$ and Pd/$LaFe_xCo_{1-x}O_3$ [23-25] corresponding to a possible stabilization of oxidic palladium species in unusual oxidation states and then exhibiting a high activity in NO_x conversion. A comparative investigation of Pt/Al_2O_3 and Pt/$LaFeO_3$ [26] also highlighted the same trend associated to the formation of Pt particles in strong interaction with $LaFeO_3$ providing a remarkable activity of Pt/$LaFeO_3$ compared to Pt/Al_2O_3 in the selective reduction of NO by H_2 at low temperature. Unfortunately, the simultaneous removal of N_2O is unable at low temperature and needs to heat the exhaust gas at more elevated temperature. Hence, based on these observations, the previous concept associated to the synthesis of smart catalysts involving reversible dynamic behaviours with noble metals going out and inside the perovskite structure during rich/lean oscillations can be revisited depending on the reducibility of the perovskite structure and the redox properties of PGM [24].

It will be show in this present study that the stabilisation of low amount of noble metals on mixed metal oxides is possible maintaining a high density of active sites at the surface through appropriate pre-activation thermal treatments. In such configuration, these optimized catalysts can be utilized both for high, moderate or low temperature applications depending on the protocol used for PGM addition and the nature of the pre-activation thermal treatment. The abatement of N_2O from acid nitric plant offers an excellent example to combine these different approaches through the sequential catalytic abatement of NO_x and N_2O (in the absence of reducing agent). Two different modes of noble metal incorporation will be investigated via sol-gel to and wet impregnation depending on the running temperature of the catalytic application showing through appropriate redox thermal treatments extensive surface reconstructions leading to a densification of surface active sites remaining stable under running conditions with enhanced catalytic properties. As a conclusion, a combined approach seems possible to reduce selectively N_2O at high temperature and efficiently NO at low temperature.

2. Experimental

2.1. Catalyst preparation and characterization

Stoichiometric perovskite-based catalysts ($LaCoO_3$ and $LaCo_{0.95}Pd_{0.05}O_3$) used for high temperature application were prepared according to a conventional sol–gel method via a citrate route [23]. Solid precursors obtained after drying overnight at 80°C were calcined in air at 900°C for 8 hours. For end-of-pipe technology, $LaFeO_3$, prepared according to the same protocol, was calcined at 600°C to maintain higher specific surface area. $LaFeO_3$ (25 m^2g^{-1}), was impregnated by hexachloroplatinic acid solutions with adjusted concentration in order to obtain 1 wt.% Pt. The impregnated precursors were successively calcined in air at 400°C and reduced at 300°C or 500°C in pure H_2.

Specific surface areas were determined by N_2 physisorption at -196°C with Quantasorb Quantachrome device. Powder X-ray diffraction (XRD) was performed at room temperature (RT) using a Bruker AXS D8 Advance diffractometer working in Bragg–Brentano geometry and equipped with a LynxEye Super Speed detector. Data were collected with Cu $K\alpha$ (λ =

0.154 nm) in the 10–70° 2θ range with a 0.02° 2θ step. The Fullprof Suite program [27] was used for Rietveld refinement. The Thompson-Cox-Hastings pseudo-Voigt function was chosen for the peak profiles. LaB_6 was used as standard to derive the instrument resolution. An isotropic size parameter of Gaussian character was refined to take into account the contribution of samples in the broadening of Bragg peaks. XPS experiments were performed using an AXIS Ultra DLD Kratos spectrometer equipped with a monochromatized aluminium source (150 W) and charge compensation gun. The analyzer was operated in a constant pass energy mode (E_{pass} = 40 eV). All binding energies (B.E.) were referenced to the C 1s core level at 285 eV. The peak areas were estimated after subtracting backgrounds according to the procedure suggested by Shirley [28]. A special attention was required for the estimate of surface atomic Co/La and Fe/La ratios after the subtraction of the Auger contributions from Fe and Co respectively. H_2 chemisorption were carried out in a Micromeritics Autochem II 2920 with 5 vol.% H_2 in Ar using a pulse technique on pre-reduced sample in H_2 at 300°C or 500°C. Metal dispersions were estimated assuming H/Pt = 1. High resolution transmission electron microscopy (HRTEM) studies were performed on a geometrical aberration corrected FEI Titan 80-300 microscope. Prior to TEM observations, samples were deposited from ethanolic solution onto holey-carbon copper grids.

2.2. Catalytic measurements

Catalytic decomposition of N_2O was studied in a fixed-bed flow reactor in temperature-programmed conditions (20–900°C, 2°C/min) using 0.7 g of catalyst. The total flow rate was adjusted to 15 $L.h^{-1}$. The reactant mixture was composed of 0.1 vol.% N_2O, 5 vol.% NO, 6 vol.% O_2, 15 vol.% H_2O diluted in He. The concentration of N_2O was measured with a dispersive IR analyzer for N_2O detection (Emerson XStream). Part of effluents was then diluted eleven-fold by means of mass flow controllers before quantification of NO and NO_2 with a chemiluminescence NO_x analyzer (Thermo 42i-HL). N_2O conversion was calculated according to Eq. (1) with $F_{N2O,\ inlet}$ and $F_{N2O,\ outlet}$ standing for respectively inlet and outlet molar flow rates of N_2O.

$$X_{N_2O} = \frac{F_{N_2O,\,inlet} - F_{N_2O,\,outlet}}{F_{N_2O,\,inlet}} \qquad (1)$$

For NO reduction at low temperature, the procedure was described elsewhere [26]. Temperature-programmed experiments were performed from RT to 500°C C in the presence of 1000 ppm N_2O, 1000 ppm NO, 3 vol.% O_2, 0.5 vol.% H_2O et 0.5 vol.% H_2 with the same weight of catalyst and total flow rate. Inlet and outlet gas mixtures were analyzed by μGC Varian CP-4900 chromatograph. The specific rate and selectivity to N_2O production were calculated from Eqs. (2) and (3) respectively were X_{NO}, m, and $F_{NO,inlet}$ stand for the conversion, m the weight of catalyst and the inlet NO flow rate.

$$r = \frac{F_{NO,\,inlet} X_{NO}}{m} \qquad (2)$$

$$S_{N_2O}\,(\%) = \frac{F_{N_2O,\,outlet}}{F_{N_2O,\,outlet} + F_{N_2,\,outlet}} \times 100 \qquad (3)$$

The experimental procedure is displayed in Scheme 1. As illustrated, all catalysts were initially pre-reduced at 300°C (or 500°C) prior to a first TPR-1 in the operating conditions above-mentioned. For this first step, the catalysts were labeled Pt/LaFe(RX), were X is the selected reduction temperature. At the final temperature reached during TPR-1, catalysts were maintained overnight under steady-state reaction conditions. After cooling down at RT, they were submitted to a post-reductive thermal treatment in H_2 similarly to the pre-reductive one and a second temperature experiments (TPR-2) was successively achieved. The catalysts submitted to this sequential processes were labeled Pt/LaFe(RXA500RX).

3. Results and discussion

3.1. High temperature N_2O decomposition on $LaCo_{1-x}Pd_xO_3$ (with $x = 0$ and 0.05)

3.1.1. In situ XRD investigation of reconstruction of perovskite $LaCo_{1-x}Pd_xO_3$ under reductive and oxidative atmospheres – impact of water

Preliminary *in situ* XRD measurements under controlled atmospheres were achieved on $LaCo_{0.95}Pd_{0.05}O_3$ prepared via a sol-gel route and calcined in air at 600°C. Elemental analysis did not reveal significant deviation compared to the theoretical composition ± 5%. Partial substitution of Pd did not lead to bulk detectable impurities related to cobalt oxide segregation due to demixing processes. It was checked that the typical rhombohedral structure for $LaCoO_3$ was maintained after Pd incorporation. The Rietveld refinement method allows the calculations of structural parameters collected in Table 1 showing an elongation of the distance *a* and parallel expansion of the elementary cell volume. Such trends are consistent with a higher ionic radius of Pd^{2+} compared to Co^{3+} cations (0.86 Å vs. 0.61 Å for Co^{3+}) [29]. *In situ* XRD measurements were performed under reductive (3 vol.% H_2 diluted in He) at 500°C and oxidative conditions in air at 800°C as described in Fig. 2A. An important outcome is provided by this preliminary study related to *in situ* measurements in the presence and in the absence of 3 vol.% H_2O. This is an important aspect because Pd modified-$LaCoO_3$

can undergo detectable structural rearrangements from XRD analysis with different kinetics, depending on the preexisting nanostructure that controls the resistance to change driven by the chemical potential of the reactants in the gas phase as stated elsewhere [30]. As previously found [11] on $LaCoO_3$ and $LaMnO_3$, hydrothermal treatments may drastically modify the structural and textural properties. Fig. 2.B illustrates structural changes on $LaCo_{0.95}Pd_{0.05}O_3$ exposed to H_2 flowing in helium. Exposure at 500°C leads to the disappearance of all the characteristic reflections of the rhomboedral structure of $LaCo_{0.95}Pd_{0.05}O_3$ under dry atmosphere. The most important change is related to the appearance of La_2O_3 exhibiting a cubic structure. Additional weak and broad reflections arise centered at $2\theta = 46°$ and 39° ascribed to metallic Co et Pd phases. These observations are consistent with H_2-TPR consumption profile in Fig. 3 emphasizing the fact that a complete reduction of Co^{2+} to Co^0 can occur more readily after Pd incorporation. Water addition during XRD experiments leads to the coexistence of the hydroxide $La(OH)_3$ precursor and the hexagonal structure of La_2O_3. However, the most prominent information could be, in that case, the lack of observation of bulky Pd and Co species which could suggest the formation of undetectable nano crystalline domains from XRD analysis including Pd.

After cooling down at RT, the sample was heated up to 800°C in air and maintained at steady state conditions for 2 hours. XRD patterns were recorded at several temperatures during the heating ramp with a temperature gradient of 5°C/min (Figure 2C). Under dry conditions, reflections observed on the reduced samples persist up to 500°C indicating no significant transformation into crystalline phases with only slightly discernible shifts which could be related to strain/disorder induced by surface reconstructions. The characteristic reflections of the rhomboedral structure appear above 700°C indicating a partial bulk reconstruction of $LaCoO_3$ still co-exiting with La_2O_3 after 10 hours thermal treatment in dry conditions at 800°C. Different behavior is remarkable in the presence of water when the re-oxidation takes place with first a broadening of the reflections ascribed to La_2O_3 and more importantly a reconstruction starting at lower temperature and being complete at much lower temperature (600°C). Structural parameters have been calculated using the Rietveld method. Their comparison in Table 1 indicates that the redox thermal treatments lead inevitably to a crystallite growth less accentuated when the reoxidation is performed in the presence of water. However, the most important information resides in the comparison of the distance *a* calculated on $LaCo_{0.95}Pd_{0.05}O_3$ becoming after reduction/reoxidation comparable to that obtained on $LaCoO_3$ suggesting during the reconstruction of the perovskite structure a preferential segregation of Pd as undetectable PdO_x species upon $LaCoO_3$ rather than re-insertion of ionic Pd species in B site of the perovskite structure. Such observation differs from that earlier reported in milder conditions demonstrating the self-regenerative behavior of noble metal modified-perovskites in three-way conditions. Indeed, such processes are likely restricted to the surface when the richness oscillates. It is worthy to note that in our case more severe conditions lead to a bulky reduction from which a complete re-incorporation of Pd in the framework of the perovskite will not be promoted during the re-oxidation step. Incomplete re-oxidation in dry conditions likely leads to more complex surface chemistry with different types of interactions with $LaCoO_3$ and La_2O_3 and or CoO_x micro domains. Separate experiments consisting of submitting calcined $LaCo_{0.95}Pd_{0.05}O_3$ to similar oxidative thermal treatment at 800°C show that the perovskite structure is preserved but a contraction of the parameter *a* is also observed which suggests a partial exclusion of isolated Pd^{2+} into undetectable bulk species possibly segregating into PdO_x aggregates.

3.1.2. Influence of bulk and surface reconstruction on the kinetics of the decomposition of N_2O on $LaCo_{0.95}Pd_{0.05}O_3$

On the basis of previous *in situ* XRD observations, illustrated in Fig. 2, different strategies were implemented for the thermal activation of $LaCo_{0.95}Pd_{0.05}O_3$ with the aim to preserve the structural properties of the perovskite structure and to increase the density of Pd sites with appropriate thermal treatments then becoming more resistant to sintering processes through stronger interactions with the perovskite structure. The description of these different *ex situ* thermal treatments is reported in Scheme 2. Catalytic measurements will be discussed in terms of normalized rate and surface Pd concentration in order to characterize the presence of synergistic effects and if specific interactions are prerequisite.

Bulk and surface composition from XPS analysis

As illustrated in Table 2, the same trends as those reported from *in situ* XRD measurements are still discernible with a contraction of the distance *a* and an increase of the crystallite size observed on LCP-4-LCP6 samples after *ex situ* reductive/oxidative thermal treatments. La 3d, Co 2p, Pd 3d and O 1s photopeaks were examined from XPS analysis. Regarding La 3d core level, B.E. values remains unchanged at 833.3 eV characterizing La^{3+} stabilized inside the perovskite structure [31]. Significant shift to higher B.E. values (834.4 eV) was observed on pre-reduced LCP-2 and LCP-6 (see scheme 2) samples consistent with the formation of La_2O_3 or $La(OH)_3$ [32] (not shown) in agreement with XRD analysis showing the disappearance of the rhomboedral structure. B.E. values recorded on the Co $2p_{3/2}$ photopeak near 780 eV accompanied with a shake-up structure at 789.5 eV characterizing the presence of Co^{3+} in LCP-0. Correlatively to previous observations on pre-reduced samples significant changes occur essentially on the shake-up structure shifting from 789.5 to 786.0 eV on LCP-3 and LCP-6 which can be related to an extensive reduction of Co^{3+} into Co^{2+} likely stabilized to CoO ou Co_3O_4 phases (not shown) after the destruction of the perovskite. While no significant shift is observed on the B.E. value of Co $2p_{3/2}$ core level, the larger Full Width at Half Maximum values recorded on LCP-3 and LCP-6 (> 3 eV) suggests the presence of metallic Co^0 species. As previously seen, subsequent oxidative thermal treatment leads to the restoration of the perovskite structure with the observation of quasi-similar B.E. values for La 3d and Co 2p core levels. It is also obvious that semi-quantitative analysis does not reveal significant deviation on the atomic Co/La and O/La ratio varying within the margin of error. The examination of the Pd 3d photopeaks in Fig. 4 shows that the Pd $3d_{5/2}$ contribution on calcined sample at 600°C (LCP-0) is symmetric with a maximum centered at 337.3 eV and Full Width at Half Maximum (FWHM) of 1.5 eV which reflect the presence of unique Pd species. B.E. seems abnormally high compared to reference values reported for PdO around 336.8 eV [33]. Such differences seem consistent with Pd^{2+} species in octahedral sites different than the tetrahedral coordination of palladium in PdO. Alternative explanation provided by Uenishi et al. [19] in $LaFePdO_x$ privileges the stabilization of Pd(III) in unusual oxidation sites. Theoretical calculations also revealed that Pd in $LaPd_{0.95}Co_{0.5}O_3$ perovskite is trivalent, providing justification for the present results [18]. However, such an explanation is not univocal since Hamada et al. did not verified from DFT calculations the stabilization of trivalent Pd species especially inside the perovskite structure [34]. As exemplified, successive redox treatments lead to comparable B.E. values for Pd $3d_{5/2}$ core level except on LCP-3 for which a lower value is reported in Table 3 accompanied with a larger FWHM which could correspond to the segregation of different oxidic Pd species. Semi-quantitative analysis reveals an increase of the surface Pd concentration when the catalyst in exposed to air at 800°C in the presence of 3 vol.% H_2O. This observation seems in relative good agreement with XRD analysis with a partial extraction of Pd^{2+} then segregating upon the perovskite surface. Successive reductive/oxidative thermal treatments accentuate this tendency except on LCP-4 with a lower Pd concentration than on LCP-1. This seems to corroborate the lowest B.E. value, closer to those currently reported for PdO, which likely reflects weaker interactions when the perovskite is not totally reconstructed.

As a general trend, the shift observed on the Pd 3d photopeak to higher B.E. values has been previously reported by Otto et al. [35]. These authors ascribed this shift to the presence of small Pd particles segregated on alumina with energy gap correlated to particle size after oxidative treatment in O_2 at 600°C. 336.5 eV was recorded when large PdO aggregates predominate and a shift of approximately 1.6 eV would correspond to redispersion into small PdO_x clusters which seems in relative agreement with our observations on LCP-4 and LCP-5. On the basis of XPS and XRD observations, it seems obvious that sequential reductive/oxidative treatment leads to reversible structural observations associated to the destruction/reconstruction of the rhomboedral structure of the perovskite. However, irreversible changes seem to characterize palladium species. Indeed, further comparisons between Rietveld refinement and XPS data clearly suggest a significant surface Pd enrichment.

Catalytic properties in N_2O decomposition vs. surface composition

Let us now examine the catalytic properties induced by Pd in different coordination and corresponding to different degree of dispersion. The comparison of the light-off temperature (T_{50}), from Temperature-Programmed conversion profiles (not shown), in Table 4 shows that LCP-5 exhibits the highest activity in N_2O decomposition related to the lowest temperature at half conversion (T_{50}) especially compared to that recorded on the parent material LCP-0. This is consistent with the normalized rate values highlighting the highest intrinsic rate value on LCP-5 for which the highest surface Pd concentration is obtained as exemplified in Fig. 5. Apparent activation energies and pre-exponential factor have been estimated from the slope and the intercepts of the Arrhenius plots respectively (see Fig. 6). Estimates reported in Table 4 reveal that the highest normalized rate on LCP-5 can be correctly explained by a sharp decrease of E_{app}. A compensation effect is also observed as discussed elsewhere on $LaCo_{1-x}Fe_xO_3$ [13] with a parallel increase of the pre-exponential factor (A) with the apparent activation energy values (see Fig. 5.a). It is worthwhile to note that rate values reported in Table 4 cannot be correlated to the elongation of the distance *a* which would mean that bulk diffusion would not be involved at moderate temperature (T = 500°C). Hence, catalytic measurements would mostly depend on the structure of topmost surface or beneath the topmost surface as reported elsewhere [34]. The origin of this compensation effect is not easy to understand being at least partly related to the explanations provided by Kondratenko et al. on $BaFeAl_{11}O_9$ and Fe-MFI [36]. Indeed, these authors suggested that the degree of clustering of FeO_x strongly influences the collision frequency of N_2O and the activation energy. This means that in our case small PdO_x clusters could originate a sharp decrease in E_{app} but would lower the probability of collision. Alternately, one cannot rule out the involvement of anionic vacancies as active sites with Pd enhancing the oxygen mobility. Taking into account the low Pd concentration compared to Co and assuming a greater Pd dispersion on LCP-5 than on LCP-4 and LCP-6 then the lower pre-exponential of LCP-5 could be related to the dependence of the distance between two Pd-O center to accelerate the recombination of atomic oxygen species as previously explained by Smeet et al. [37]. As a matter of fact, Hamada et al. [34] provided an explanation from DFT calculations on $LaFe_{1-x}Pd_xO_3$ that can reconcile all these interpretations and which can be extrapolated to $LaCo_{1-x}Pd_xO_3$ even if its reducibility strongly differs. In fact, these authors suggested a possible self-regeneration mechanism for $LaFe_{1-x}Pd_xO_3$ involving anionic vacancies V_O forms at a subsurface site beneath the surface M metal which would promote surface segregation of Pd atoms then forming $LaPdO_{3-y}$ in the vicinity of the $LaFe_{1-x}Pd_xO_3$ surface. The lower formation energy of 1.52 eV for subsurface V_O compared to an isolated O_2 molecule (2.13 eV for clean $LaFeO_3$) would stabilize the surface segregation of the precious metal. Hence, calcination of $LaCo_{1-x}Pd_xO_3$ at 800°C in air likely favor the partial desorption of oxygen and the creation of anionic vacancies that can destabilize the structure and promote clustering effects of PdO_x in strong interaction with $LaCoO_3$ and $LaCo_{1-x}Fe_xO_3$.

3.2. Low temperature NO reduction on 1 wt.% Pt/LaFeO₃

3.2.1. Influence of pre-reductive thermal treatment on the extent of surface reconstruction under reaction conditions at 500°C on 1 wt.% Pt/LaFeO₃

As earlier found, aging under oxidative conditions led to redispersion of Pt on 1 wt.% Pt/$LaFeO_3$ [38]. X-ray photoelectron spectroscopy helped to understand such processes but analysis on a depth of approximately 5-10 nm can only provide an average tendency regarding the occurrence of agglomeration or re-dispersion processes. This was in fact the meaning of previous observations showing through the calculation of the atomic Pt/Fe ratio an increase of the surface Pt concentration after exposure to oxidative conditions under reaction mixture and a decreasing concentration when the samples were exposed to reductive atmosphere. Pt particle size distribution obtained by TEM analysis of Pt supported on $LaFeO_3$, after thermal treatments at 300 and 500°C, demonstrated the formation of smaller particles [38]. On Pt/LaFe(R300), small Pt particles were present with a mean diameter of 1.0 nm. Subsequent thermal aging treatment led to an enlargement of the particle diameter with a mean value of 1.8 nm. A redispersion process occurred after the post-reductive thermal treatment in H_2 highlighted by a decrease of the mean particle size from 1.8 to 1.2 nm. A similar behaviour was observed on the samples treated in pure H_2 at 500°C during the reducing step with an enlargement of the particle size during aging (1.3 nm for Pt/LaFe(R500) and 1.5 nm for Pt/LaFe(R500A500) followed by a redispersion after subsequent reduction with a mean particle size of 1.1 nm on Pt/LaFe(R500A500R500). Overall, TEM observations confirmed the absence of sintering phenomenon on platinum when supported on $LaFeO_3$ throughout the thermal treatment process whatever the temperature of the reducing step. However, they cannot be straightforwardly related to change in activity without information on the density of metallic Pt sites at the surface and on the nature of the metal/support interface. To this purpose, additional H_2 and CO titrations were achieved on $Pt/LaFeO_3$ catalysts from which the Pt dispersion can be estimated and compared as shown in Table 5. As exemplified, the same tendency is confirmed as earlier found on $Pt/LaFeO_3$ ascribed to a redispersion of accessible Pt sites after ageing and post-reductive H_2 treatment. Estimates of the normalized rates expressed per surface atom will be discussed later.

Further investigation was performed in this study by HRTEM and Figs 7 and 8 show representative images obtained on these samples. On all images, the orthorhombic phase of $LaFeO_3$ was identified from measurements of the lattices fringes of the (0 0 2), (1 1 1), (2 0 0) and (2 0 2) crystal planes characteristic of this structure (respectively, 3.93 Å, 3.51 Å, 2.78 Å and 2.27 Å). Platinum particles were also observed, with measured lattice fringes corresponding to the (1 1 1) planes of metallic platinum (2.27 Å). Among the observed particles, HRTEM micrographs recorded on Pt/LaFe(R300) show a preferential orientation of the (1 1 1) crystal planes of the Pt particles, anchored to the different (2 0 0), (1 1 1), (0 0 2) and (2 0 2) planes characteristic of $LaFeO_3$ structure (see Fig. 7). Similar observations were repeated on Pt/LaFe(R300A500R300) which emphasises the fact that these metallic Pt particles strongly interact with the support even after subsequent thermal treatments.

On the other hand, these interactions were not observed on Pt/LaFe(R500) and Pt/LaFe(R500A500R500), as illustrated in Fig. 8, showing at each step of the thermal treatment metallic Pt particles with random orientation towards the perovskite support. It clearly appears that H_2 reduction at 500°C suppresses the interaction previously observed at 300°C.

3.2.2. Influence of thermal reductive/oxidative treatment on the catalytic reduction on NO on 1 wt.% Pt/LaFeO$_3$

Earlier results obtained on 1 wt.% Pt/LaFeO$_3$ reported elsewhere [37] have been used for the calculation of new data allowing the calculation of turn-over-number from Pt dispersion reported in this paper (see Table 5). Two distinct temperature ranges for NO conversion were previously evidenced, with maximum conversion usually recorded below 200°C. However, these maximum conversion were found to be sensitive to the temperature of the pre-reductive treatment in H$_2$ with a detrimental effect when this one is performed at 500°C i.e. 75% NO conversion at 122°C on Pt/LaFe(R300) vs. 61% at 162°C on Pt/LaFe(R500) [37]. However, the most important observation is related to the significant gain in activity obtained on aged Pt/LaFe(R300A500R300) with a complete NO conversion at a much lower temperature (113°C). Such a tendency is also observed on Pt/LaFe(R500A500R500) but in lower extent. In a first approach such observations seem consistent with the Pt redispersion observed from H$_2$ titration and previous TEM observations, this process being limited when the catalyst is pre-reduced at 500°C. However, the density of Pt sites could not be the sole parameters in determining the catalytic properties with significant changes observed in the nature of the Pt/LaFeO$_3$ interface according to the reduction temperature. From a practical view point such results open new prospects towards the reduction of noble metal content. In order to check the impact of Pt content on the extent of redispersion process and related rate enhancement we have evaluated the catalytic performances of a low loaded 0.5 wt. Pt/LaFeO$_3$ catalyst. As shown in Fig. 9, similar trends are observable with a gain in activity below 200°C on 0.5Pt/LaFe(R300A500R300) compared to 0.5Pt/LaFe(R300). On the other hand both samples behave similarly at higher temperature. This suggests that agglomeration/redispersion processes, restricted on this system to the surface, would influence the catalytic properties of Pt/$LaFeO_3$ notably at low temperature (below 200°C). To get more insights into the kinetics of the NO/H_2 reaction we have selected two characteristic temperatures for the different kinetic regimes and calculated the corresponding TOF values. First, we have selected a low temperature of 80°C for which the conversion is suppressed on Pt/LaFe(R500) and Pt/LaFe(R500A500R500) compared to Pt/LaFe(R300) and Pt/LaFe(R300A500R300). For the high temperature domain the rates have been calculated at 255°C. Rate values are compared in Table 5. It is worthy to note that despite the significant deviation in temperature the normalized rates remain of the same order of magnitude on Pt/LaFe(R300) i.e. 67 h^{-1} at 80°C vs. 110 h^{-1} at 255°C which highlights the creation of highly active sites at low temperature. However, we have also to take into account the competitive H_2/O_2 reaction becoming more significant with a rise in temperature and then lowering the amount of H_2 available for the reduction of NO. As earlier shown [37], the extent of conversion at 255°C strongly depends on the temperature of the pre-reductive thermal treatment in pure H_2. As indicated in Table 5, pre-reduction at 500°C has a strong detrimental effect on the rate of NO reduction measured at 80°C. At moderate H_2 reduction temperature (T = 300°C) the superficial structure of the perovskite should be preserved. On the other hand, the creation of defective microstructure at 500°C up to a critical level can destabilize the perovskite structure creating micro domains generating different types of interactions with Pt which could partly explain the alteration of the catalytic properties at low T. Such behavior has been already described in the previous chapter dedicated to N_2O decomposition when $LaCo_{0.95}Pd_{0.05}O_3$ is heated in air at high temperature. In this conditions, an extensive production of anionic vacancies can occur through oxygen desorption then enhancing Pd extraction and segregation. However, the most important changes on Pt/$LaFeO_3$ are related to surface reconstructions after successive reductive/oxidative thermal treatment, particularly under reaction conditions, which induce significant changes on the intrinsic properties of Pt sites based on the comparison of the TOF values in Table 5. As seen in Table 5, the comparison of the TOF values at 80°C on Pt/LaFe(R300) and Pt/LaFe(R300A500R300) shows only slight variations highlighting a weak structure-sensitivity. On the other hand, significant modifications are observable of the TOF values recorded at 255°C on Pt/LaFe(R500) and Pt/LaFe(R500A500R500) shifting from 110 to 5h^{-1}. Such a trend is also discernible when the catalyst is initially pre-reduced at 300°C but in lower extent which likely highlights the importance of the strength of the metal/support interface on the stability of nano-sized Pt particles. This comparison would suggest that the relative rates of steps taking place over Pt particles at 255°C would occur much more readily than those involving the metal/support interface then restoring the structure sensitivity of this reaction. Such a behavior could be related to the fact that on both samples reaction pathways would preferentially occur on Pt sites at high temperature whereas the metal/support interface would be involved for Pt/LaFe(R300) and Pt/LaFe(R300A500R300) at 80°C.

Commenté [P2]: Continuer avec le modèle proposer par A. Efstathiou

3.3. General assessments

Up to now most investigation emphasized the fact that the settlement of end-of-pipe technologies to treat exhaust gas from acid nitric plant is challenging because the simultaneous conversion of NO and N_2O requires more elevated temperature than that of the exhaust gas (~ 200°C). The present study confirms this tendency even if efficient noble metals stabilize on perovskite support lead to a widening of the operating window opening new strategies for reducing the content of noble metals. Previous investigation of 1 wt.% $Pt/LaFeO_3$ during the NO/H_2 reaction opened the discussion concerning the origin of two distinct conversion ranges at low and high temperature [38]. They persist on low loaded 0.5 wt. $Pt/LaFeO_3$ but only below 200°C. Such kinetic features seem closely related to the richness of the reaction mixture. Indeed, the occurrence of two different domains for NO conversion is usually observed in lean conditions (with an excess of oxygen) and could correspond to different reaction pathways as argued elsewhere [39,40]. Such existence of two NO conversion ranges has been already reported and ascribed to the involvement of different intermediates [39,40]. For instance Ueda et al. who investigated the NO/H_2 reaction on Pd/TiO_2, explained the appearance of low and high maximum NO conversion on the basis of two different routes involving respectively dissociated NO species or intermediate NO_2 formation kinetically limited at low temperature. Similar observations on Pt/$LaCeMnO_3$ [41] and Pt/MgO-CeO_2 [39] led to different interpretations. Indeed, Costa et al. proposed that the formation of ad-NO_x species at the vicinity of metallic Pt particles can react at the metal/support interface through spill-over effects with dissociated hydrogen species bounded to Pt. The extent of such spill-over processes can depend on the size of Pt particles as well as their morphology. Such a mechanistic proposal seems also in agreement with the observations reported by Okumura et al. [42] showing a rate enhancement in NO conversion when Pt is deposited on CeO_2 and ZrO_2 instead of alumina and silica for which no significant conversion is observed. Hence, the activity in NO reduction has been related to the involvement of anionic vacancies on CeO_2 and ZrO_2 located close to the noble metal particles. In our case, change in the Pt dispersion seems to have a significant effect at low temperature corresponding to a weak structure sensitivity currently ascribed to NO dissociation step. Such observation seems in line with the mechanistic scheme suggested by Costa et al. [39,41] who explained the behavior of Pt/$LaCeMnO_3$ and Pt/MgO-CeO_2 through the metal/support interface where H_2 would dissociate predominantly on Pt and then spill-over at the metal/support interface. At low temperature, NO dissociation would not be favored on Pt (111) compared to Rh and a weak inhibiting effect of NO on H_2 dissociation is also expected still in comparison with Rh. Hence, the rate enhancement observed at 80°C on

Pt/LaFe(R300A500R300) can be rationalized by the development of the metal/support interface due to Pt redispersion processes. At 255°C, the alteration of the metal/support interface especially on aged samples Pt/LaFe(R300A500R300) and particularly on Pt/LaFe(R500A500R500) is accompanied by significant changes of the TOF values which could be an indication of the restoration of the structure-sensitivity [43,44] for the NO/H_2 reaction with steps for NO transformation taking place predominantly on Pt sites.

Finally, returning to the decomposition of N_2O on $LaCo_{0.95}Pd_{0.05}O_3$, while this reaction presents different kinetic features compared to the NO/H_2 reaction taking place at much higher temperature and in the absence of reducing agent, some similarities may exist. Probably the most significant one is relied to the activation protocols which also implied redox treatments. However, those ones take place to different extent and are not restricted to the surface as in the case of Pt/$LaFeO_3$ because of the highest reducibility of $LaCoO_3$. Hence, bulk transformation leads to a significant extraction of Pd from the lattice to segregate as PdO_x clusters upon the perovskite structure once reconstructed. However, the redispersion of PdO_x could not completely explain changes in the catalytic properties as exemplified in Fig. 5.b. Indeed, previous comparisons of catalytic measurements on Pd/Al_2O_3 and Pd/$LaCoO_3$ during the decomposition of N_2O clearly showed that freshly-prepared Pd-modified perovskite was more active in spite of its lower metal dispersion (0.16 against 0.86 on Pd/Al_2O_3). This observation simply underlines the significant effect of the metal/support interaction on the catalytic performance [24]. At high temperature, with pre-activation thermal treatment performed at moderate temperature an optimal metal/support interaction could explained the peculiar behavior of $LaCo_{0.95}Pd_{0.05}O_3$ pre-reduced in H_2 at 500°C and reoxidized in air at 800°C under wet conditions which accelerates the reconstruction of the rhomboedral structure after reduction and leads to the highest surface Pd/La ratio. As a matter of fact, the involvement of the interface can be suggest on the basis of the compensation effect illustrated in Fig. 5.a which can be related to the creation of new active sites where palladium in strong interaction can weaken Co-O bond. This explanation seems in line with previous one related to the stabilization of nanostructures on Pt/CeO_2 [22] ascribed to the formation of nano composite oxides that involves the formation of a Pt–O–Ce bond. Based on this, the weakening of the Co-O bond, due to the proximity of Pd in reconstructed $LaCo_{0.95}Pd_{0.05}O_3$, is probably responsible of the lowering of the apparent activation energy whereas, according to Smeet et al. [37], the lowest value obtained on the pre-exponential factor could be related to the dependence of the distance between two (Pd)Co-O center to accelerate the recombination of atomic oxygen species.

4. Conclusion

This study deals with a combined approach to remove sequentially N_2O and NO from nitric acid plants. Precious metals were added to perovskite type materials with the aim to compensate deactivation phenomena at high temperature during the decomposition of N_2O and to promote synergistic effects at low temperature for the removal of NO. For these two reactions, the PGM/perovskite interface was found as a key parameter in determining the catalytic properties. To get an optimal performance, the methodology involving redox thermal treatments has been tentatively optimized as a function of the reducibility of the perovskite and the protocol used for noble metal incorporation. For the high temperature catalytic N_2O decomposition, Pd incorporated to $LaCoO_3$ according to a sol-gel route can migrate at the surface through oxygen desorption at 800°C with extensive defect formation which partly destabilizes the structure. More extensive surface Pd can be enhanced through reductive/oxidative treatments especially in wet conditions which speed up the reconstruction of the perovskite once reduced after H_2 exposure at 500° and then increasing the density of Pd sites at the surface. A compensation effect is observed related to the creation of active sites at the surface combining the proximity of Pd and Co and anionic vacancies.

In the particular case of the NO/H_2 reaction, Pt was added to $LaFeO_3$ through a classical wet impregnation. Redox thermal treatments involving the topmost surface due to the weak reducibility of $LaFeO_3$ were implemented to redisperse Pt species and create specific interactions capable to originate synergistic effects on the catalytic activity. As found, the nature of the interaction between Pt and $LaFeO_3$ strongly depends on the temperature of the pre-reductive thermal treatment. Pre-reduction in H_2 at 300°C leads to the growth of epitaxially Pt (111) surface parallel to the characteristic fringes of $LaFeO_3$ corresponding to a significant enhancement of the TOF at low temperature. The weak sensitivity to the structure suggests the creation of new active site at the Pt/$LaFeO_3$ interface. On the other hand, reduction at 500°C is detrimental on the activity associated to significant alteration of the metal/support interaction. In this latter case, the structure sensitivity of the NO/H_2 reaction is restored at higher temperature.

Acknowledgements

The UCCS participates in the Institut de Recherche en ENvironnement Industriel (IRENI) which is financed by the Communauté Urbaine de Dunkerque, the Région Nord Pas-de-Calais, the Ministère de l'Enseignement Supérieur et de la Recherche, the CNRS and European Fund for Regional Development (FEDER). We gratefully acknowledge the IRENI and the ADEME for financial support through a PhD fellowship (Y. Wu and J.P. Dacquin). The authors acknowledge financial support from METSA network.

Reference

[1] The Kyoto Protocol, United Nations Framework Convention on Climate Change, COP 3, Kyoto, Japan, December 11, 1997.

[2] J. Pérez-Ramiréz, Appl. Catal. B 70 (2007) 31.

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

[4] J. Pérez-Ramirez, F. Kapteijn, G. Mul, X. Xu, J.A. Moulijn, Catal. Today 76 (2002) 55.

[5] S. Alini, F. Basile, S. Blasioli, C. Rinaldi, A. Vaccari, Appl. Catal. B 70 (2007) 323.

[6] Ø. Nirisen, K. Schöffel, D. Waller, D. øvrebø, WO0202230 A1, 2002, to Norsk Hydro.

[7] P. Granger, P. Esteves, S. Kieger, L. Navascues, G. Leclercq, Appl. Catal. B 62 (2006) 236.

[8] P. Esteves, Y. Wu, C. Dujardin, M.K. Dongare, P. Granger, Catal. Today, 176 (2011) 433.

[9] W. Burckardt, M. Voigt, EP 1147813 A2, 2001, to Porzellanwerk Kloster Veilsdor.

[10] J. Neumann, L. Isopova, L. Pinaeva, N. Kulikovskaya, L. Zolotarskii, WO2007104403 A1), 2007, to Umicore.

[11] V.R. Choudhary, S. Banerjee, B.S. Uphade, Appl. Catal. A 197 (2000) 183.

[12] G.L. Chiarello, J.-D. Grunwald, D. Ferri, F. Krumeich, C. Oliva, L. Forni, A. Baiker, J. Catal. 252 (2007) 127.

[13] Y. Wu, C. Cordier, E. Berrier, N. Nuns, C. Dujardin, P. Granger, Appl. Catal. B 140-141 (2013) 151.

[14] S. Imamura, R. Hamada, Y. Saito, K. Hashimoto, H. Jindai, J. Mol. Catal. A 139 (1999) 55.

[15] A. Bueno-López, I. Such-Basáñez, C. Salinas-Martínez de Lecea, J. Catal. 244 (2006) 102.

[16] X. Zhao, Y. Cong, Y. Huang, S. Liu, X. Wang, T. Zhang, Catt. Lett. 141 (2011) 128.

[17] X. Zhao, Y. Cong, F. Lv, L. Li, X. Wang, T. Zhang, Chem. Comm. 46 (2010) 3028.

[18] Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto, N. Hamada, Nature, 418 (2002) 164.

[19] M. Uenishi, M. Tanigushi, H. Tanaka, M. Kimura, Y. Nishihata, J. Mizuki, T. Kobayashi, Appl. Catal. B, 57 (2005) 267.

[20] H Taguchi, S.I. Matsu-ura, M. Nagao, T. Choso, K. Kabata, J. Solid State Chem. 129 (1997) 60.

[21] M. Uenishi, H. Tanaka, M. Tanigushi, I. Tan, M. Kimura, Y. Sakamoto, S. Matsunaga, K. Yokota, T. Kobayashi, Appl. Catal. A, 296 (2005) 114.

[22] M. Hatanaka, N. Takahashi, N. Takahashi, T. Tanabe, Y. Nagai, A. Suda, H. Shinjoh, J. Catal. 266 (2009) 182.

[23] I. Twagirashema, M. Engelmann-Pirez, M. Frere, L. Burylo, L. Gengembre, C. Dujardin, P. Granger, Catal. Today 119 (2007) 100.

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

[25] I. Twagirashema, M. Frere, L. Gengembre, C. Dujardin, P. Granger, Top. Catal. 42–43 (2007) 171.

[26] J.P. Dacquin, C. Lancelot, C. Dujardin, C. Cordier-Robert, P. Granger, J. Phys. Chem. 115 (2011) 1911.

[27] J. Rodriguez-Carjaval, Physica B 192 (1993) 55; J. Rodríguez-Carvajal, Commission on Powder Diffraction (IUCr) Newsletter, 26, 2001, pp. 12.

[28] D.A. Shirley, Physical Review B 5 (1972) 4709.

[29] R.D. Shannon, Acta Crystallogr. A 32 (1976) 751.

[30] R. Schlögl, Adv. Catal. 52 (2009) 273.

[31] H. Taguchi, S. Yamada, M. Nagao, Y. Ichikawa, K. Tabata, Mater. Res. Bull. 37 (2002) 69.

[32] M.F. Sunding, K.Hadidi, S. Diplas, O.M. Løvvik, T.E. Norby, A.E. Gunnæs, J. Electron Spectrosc. and Relat. Phenom. 184 (2011) 399.

[33] D. Briggs, M.P. Seah, In Practical Surface Analysis (2nd ed.), vol.1, John Wiley: Chichester, 1999, pp. 599.

[34] I. Hamada, A. Uozumi,‡ Y. Morikawa, A. Yanase, H. Katayama-Yoshida, J. Am. Chem. Soc. 2011, 133, 18506.

[35] K. Otto, L.P. Haack, J.E. deVries, Appl. Catal. B 1 (1992) 1.

[36] E.V. Kondratenko, V.A. Kondratenko, M. Santiago, J. Pérez-Ramirez, Appl. Catal. B 99 (2010) 66-73; J. Catal. 256 (2008) 248.

[37] P.J. Smeets, B.F. Sels, R.M. van Teeffelen, H. Leeman, E.J.M. Hensen J. Catal. 256 (2008) 143.

[38] J.P. Dacquin, C. Lancelot, C. Dujardin, C. Cordier-Robert, P. Granger, J. Phys. Chem. C 115 (2011) 1911.

[39] C.N. Costa, A.M. Efstathiou, J. Phys. Chem. C 108 (2007) 3010.

[40] A. Ueda, T. Nakano, M. Azuma, T. Kobayashi, Catal. Today, 45 (1998) 135.

[41] C.N. Costa, A.M. Efstathiou, J. Phys. Chem. B 108 (2004) 2620.

[42] K. Okumura, T. Motohiro, Y. Sakamoto, H. Shinjoh, Surf. Sci. 603 (2009) 2544.

[43] C.H.F. Peden, D.N. Belton, S.J. Schmieg, *J. Catal.* 155 (1995) 204.

[44] D.N. Belton, C.L. DiMaggio, S.J. Schmieg, K.Y.S Ng, J. Catal. 157 (1995) 559.

Figure captions

Fig. 1. Simplified scheme of an industrial plant for acid nitric production.

Fig. 2. Temperature-programmed *in situ* XRD measurements on $LaCo_{0.95}Pd_{0.05}O_3$ – (A) Scheme of the temperature profiles of the sequential thermal treatments – (B) Reductive thermal treatment in 3 vol.% H_2 after exposure to RT (a), at 500°C (b) and after cooling down at RT – (C) Oxidative thermal treatment in air – (#) Rhombohedral $LaCo_{1-x}Pd_xO_3$; (○) Cubic La_2O_3; (●) Pd^0; (◇) hexagonal La_2O_3; (◆) hexagonal $La(OH)_3$.

Fig. 3. H_2-Temperature programmed experiments performed on $LaCoO_3$ and $LaCo_{0.95}Pd_{0.05}O_3$ exposed to 5 vol.% H_2 in Ar and a heating rate of 2°C/min.

Fig. 4. XPS Pd $3d_{5/2}$ photopeak recorded on $LaCo_{0.95}Pd_{0.05}O_3$ submitted to various redox thermal treatments as described in Scheme 2.

Fig. 5. Compensation effect (a) and correlation between normalized rates recorded on $LaCo_{0.95}Pd_{0.05}O_3$ during the decomposition of N_2O at 500°C with surface Pd concentration calculated from XPS measurements (b) – Reaction conditions : 0.1 vol.% N_2O, 5 vol.% NO, 6 vol.% O_2, 15 vol.% H_2O diluted in He

Fig. 6. Arrhenius plots recorded on $LaCo_{0.95}Pd_{0.05}O_3$ submitted to various redox thermal treatments as described in Scheme 2 – Reaction conditions : 0.1 vol.% N_2O, 5 vol.% NO, 6 vol.% O_2, 15 vol.% H_2O diluted in He.

Fig. 7. HRTEM images of (a) Pt/LaFe(R300) and (b) Pt/LaFe(R300A500R300).

Fig. 8. HRTEM images of (a) Pt/LaFe(R500) and (b) Pt/LaFe(R500A500R500).

Fig. 9. Influence of the pre-reductive thermal treatment on 0.5 wt.% Pt/$LaFeO_3$ on the Temperature-Programmed NO conversion curves: 0.5Pt/LaFe(R300) (○) and 0.5Pt/LaFe(R300A500R300) (●) – Reaction conditions : 1000 ppm N_2O, 1000 ppm NO, 3 vol.% O_2, 0.5 vol.% H_2O et 0.5 vol.% H_2 diluted in He.