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Investigation of the catalytic performances of supported noble metal based catalysts in the NO + H_2 reaction under lean conditions

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Abstract

This paper compares the catalytic performances of various supported palladium and platinum catalysts on a conventional γ-Al_2O_3, and $LaCoO_3$ perovskite that exhibits peculiar redox properties in the reduction of NO by hydrogen under lean conditions. A particular attention has been paid towards the catalytic behaviour of noble metals at low temperature, mainly below 120 °C. Clearly, their catalytic properties in the selective reduction of NO into N_2 strongly depend on the feed gas composition, and on the nature of the support. In that temperature range, Pt/Al_2O_3 exhibits the better activity, unfortunately undesirable N_2O is predominantly formed. The most prominent results have been obtained on $Pd/LaCoO_3$ because H_2O promotes the reduction of NO without affecting the selectivity behaviour, whereas a strong inhibiting effect on the rate of NO transformation into N_2 is observed on Pd/Al_2O_3. Such differences in the catalytic behaviour of palladium could be related to different interactions between Pd and $LaCoO_3$ generated during the activation thermal treatment under reductive atmosphere.

Keywords: Noble metals; NO reduction; N_2O selectivity; $LaCoO_3$ perovskite

1. Introduction

Presently, the selective reduction of nitric oxides (NO_x) using ammonia as reducing agent is widespread through the world, this technology being the most powerful for reducing selectively NO into N_2 under lean conditions between 200 and 400 °C. On the other hand, at higher temperature, the competitive oxidation of NH_3 usually takes place. Furthermore, restrictive standard regulations on the emissions of atmospheric pollutants should concern an increasing number of industrial plants. Hence, the implementation of these new restrictions should generate significant improvements on the performances of the existing catalytic exhaust systems. The reduction of nitric oxide under lean conditions using ammonia as reducing agent on typical vanadia-titania based catalysts is less efficient for low temperature exhaust gases. In that particular case, the catalytic reduction with hydrogen seems to be a promising technology, although H_2 is usually recognised as none selective. In addition, the formation of undesirable N_2O usually predominates. Recent investigations [1–4] show that supported noble metal based catalysts can profitably be used for reducing more selectively NO into N_2 in the presence of O_2. It is found that the extent of interaction between the metal and the support governs the activity and the selectivity behaviour of noble metals. The most significant results have been obtained on Pt that usually exhibits poorer efficiency than Rh in the dissociation of NO [1].

This paper reports a study on the influence of oxygen and water on the catalytic performances of Pd and Pt supported on $LaCoO_3$ and alumina. This comparison shows that the use of palladium supported catalysts has to be considered, especially when $LaCoO_3$ is used as support.

2. Experimental

$LaCoO_3$ perovskites were prepared using a so-called sol–gel method involving a citrate route [5]. Aqueous solutions of $La(NO_3)_3 \cdot 6H_2O$ (Fluka) and $Co(NO_3)_2 \cdot 6H_2O$ (Fluka)

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were mixed with a solution of citric acid (Fluka) with a molar citric acid/(La + Co) ratio of 1. After evaporation the gel thus obtained was dried overnight. Finally, the resulting material was calcined in flowing air at 600 °C for 5 h for obtaining the rhombohedral structure of $LaCoO_3$. The supported noble metal based catalysts were prepared according to a conventional wet impregnation method using palladium nitrate and hexachloroplatinic acid solutions with adjusted concentrations in order to obtain 1 wt.% Pt or Pd. After impregnation on γ-alumina (100 $m^2 g^{-1}$) and $LaCoO_3$ (20 $m^2 g^{-1}$), the samples were calcined in air at 400 °C for 2 h, and then reduced at 250 or 500 °C in pure H_2.

The structural properties were studied by XRD on a D5000 diffractometer using Cu Kα ($\lambda = 1.54056$ Å) radiation. Temperature-programmed reduction (TPR) was carried out in a Micromeritics Autochem II 2920. Surface compositions were obtained by XPS analyses using a Leybold Heraeus spectrometer. Binding energy levels were referenced to the C 1s binding energy level at 285 eV. Catalytic performances were evaluated from temperature-programmed experiments performed in a fixed-bed flow reactor between 25 and 500 °C with a constant heating rate of 2 °C min^{-1}. Typically, the mass of catalyst was 0.7 g and the global flow rate was adjusted in order to obtain a space velocity of 4000 h^{-1}. The effluents were analysed by a Balzers mass spectrometer and a HP 5890 series II chromatograph fitted with a thermal conductivity detector. Before quantification, products and reactants were separated on a CTR1 column from Alltech.

3. Results and discussion

3.1. Physico-chemical properties of $LaCoO_3$ before and after subsequent addition of noble metals (Pt and Pd)

Fig. 1 illustrates structural changes of $LaCoO_3$ during H_2 exposure from room temperature to 800 °C. The X-ray diffraction pattern recorded on $LaCoO_3$ at 20 °C exhibits the characteristic X-ray lines of the typical rhombohedral structure usually stabilised at room temperature with the most intense diffraction lines located at $2\theta = 32.9°$, 33.3° and 47.5° (see JCPDS data no. 48-0123). No significant contributions related to bulk Co_3O_4 and La_2O_3 phases are detectable. The specific area of 20 $m^2 g^{-1}$ is approximately one order of magnitude higher than those previously reported on solids obtained via a sol–gel method and calcined at a significant higher temperature of 800 °C [6]. As observed in Fig. 1, $LaCoO_3$ is unstable under reducing atmosphere at high temperature. Such typical modifications have been earlier explained in the literature [7,8]. Below 300 °C, the structural properties of $LaCoO_3$ are preserved. On the other hand, a significant shift in location of the main X-ray lines of $LaCoO_3$ occurs in the range 300–500 °C parallel to appearance of additional contributions at $2\theta = 31.5°$ and 32.5°. Above 500 °C, extensive reduction of $LaCoO_3$, evidenced by the development of X-ray lines characteristic of La_2O_3 at $2\theta = 26.2°$, 29.2°, 30°, 39.6°, 46.2°, 52.3°, 55.5° and bulk detectable metallic Co crystallites at $2\theta = 44.2°$, takes place. According to the literature data [8,9], XRD observations suggest that $LaCoO_3$ does not reduce directly to Co and La_2O_3, but probably via the intermediate formation of oxygen-deficient compounds. Also, the formation of La_2CoO_4 cannot strictly be ruled out. Such statements are supported by additional temperature-programmed reduction experiments (Fig. 2). The hydrogen consumption profile of $LaCoO_3$ in Fig. 2(a) exhibits two ranges between 200–500 and 500–730 °C with atomic H/Co ratio of, respectively, 0.98 ± 0.02 and 2.04 ± 0.02 which highlight a two-step reduction process involving the intermediate formation of Co^{2+}. Both information could be explained by the formation of an oxygen-deficient perovskite that could act as intermediate in the overall reduction process, or alternately, by different reaction paths involving the intermediate

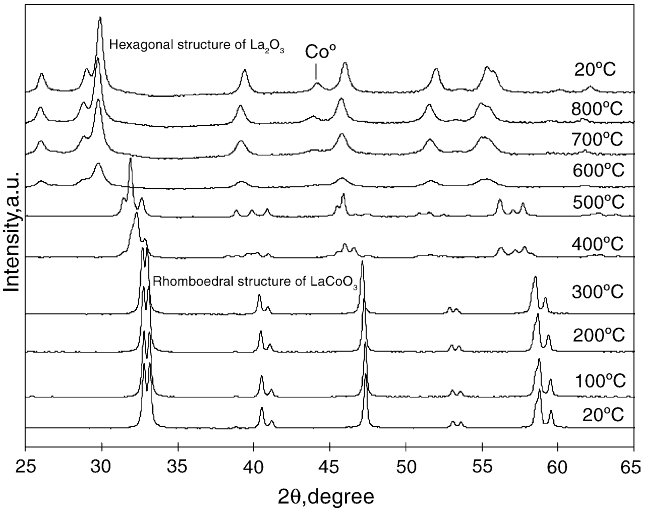

Fig. 1. XRD analysis of $LaCoO_3$ at various temperatures under pure H_2.

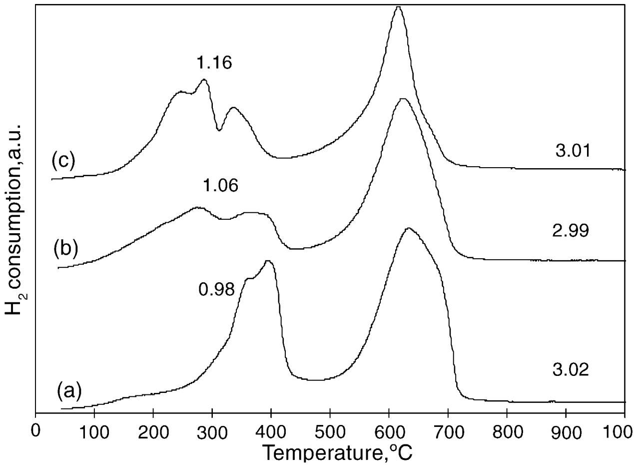

Fig. 2. Temperature-programmed reduction of $LaCoO_3$ (a), $Pd/LaCoO_3$ (b) and $Pt/LaCoO_3$ (c) in 5 vol.% H_2 diluted in He.

formation of La_2CoO_4 and CoO according to the following sequences:

First step:

$$2LaCoO_3 + H_2 \rightarrow La_2CoO_4 + CoO + H_2O \quad (1)$$

Second step:

$$La_2CoO_4 + CoO + H_2 \rightarrow La_2CoO_4 + Co + H_2O \quad (2)$$

$$La_2CoO_4 + Co + H_2 \rightarrow La_2O_3 + 2Co + H_2O \quad (3)$$

The examination of the total atomic H/Co ratio (H/Co $\cong$ 3) highlights a complete reduction of Co^{3+} into Co^0. Further addition of noble metals mainly promotes the reduction of Co^{3+} into Co^{2+}, which starts at lower temperature on Pd/$LaCoO_3$ and Pt/$LaCoO_3$, below 200 °C. The values of the atomic H/Co ratio corresponding to the first reduction step slightly higher than 1 can be explained by the reduction of PtO_2 and PdO into metallic Pt and Pd. The high temperature reduction peak is also affected by the subsequent addition of noble metals with the second reduction step starting at lower temperature.

Previous workers [10] mentioned that $LaCoO_3$ can be reversibly reduced and oxidised in mild temperature conditions, typically below 500 °C where sintering reactions are inhibited. In fact, the irreversibility of the redox cycle is closely related to the sharp increase in the crystal size of cobalt particles [10]. In our typical activation conditions under H_2 before reaction, the reduction of $LaCoO_3$ leads predominantly to the formation of undetectable cobalt species. Accordingly, the segregation of well-dispersed Co species would be favourable for the observation of such reversible changes in the course of the reaction. Additional surface characterisations by XPS (see Table 1) after in situ successive reductive–oxidative exposures, respectively, under H_2 and O_2 at 450 °C, in the temperature conditions corresponding to the first reduction peak, evidence reversible processes with the observation of Co^{2+} characterised by a binding energy (BE) of 779.5 eV after reduction in H_2, and the restoration of Co^{3+} (with BE = 780.3 eV) after subsequent air exposure. Such reversible changes could deeply influence the catalytic properties of $LaCoO_3$, previous authors stating that the presence of both anionic vacancies and Co^{2+} species originates the catalytic performances of $La_{0.9}Ce_{0.1}CoO_{3+\delta}$ [11].

Table 1
XPS investigation of modifications in surface properties of $LaCoO_3$ during a redox cycle under hydrogen (10 vol.% H_2 in N_2) and oxygen (10 vol.% O_2 in N_2) at 450 °C

	Surface stœchiometric composition	Binding energy (eV)		
		Co 2p	O 1s	La 3d
Before treatment	$LaCo_{0.74}O_{3.16}$	780.5	529.3	834
After H_2 exposure	$LaCo_{0.54}O_{2.46}$	779.5	529.1	834
After O_2 exposure	$LaCo_{0.51}O_{2.99}$	780.3	529.3	834

3.2. Catalytic NO + H_2 reaction on M/$LaCoO_3$ (with M = Pt or Pd) under lean conditions

3.2.1. Intrinsic properties of Pt, Pd and $LaCoO_3$

Preliminary temperature-programmed NO + H_2 reaction in a large excess of oxygen on pre-reduced Pd/Al_2O_3 and Pt/Al_2O_3 in H_2 are reported, respectively, in Figs. 3 and 4. They reveal complex catalytic features due to the occurrence of various competitive and successive reactions leading to the formation of N_2, N_2O and H_2O, NH_3 being not detected under our experimental conditions, with a large excess of oxygen (3 vol.%). Nevertheless, it seems obvious that supported platinum and palladium catalysts behave similarly. Clearly, two conversion ranges can be distinguished that have been earlier observed on noble metal based catalysts supported over various materials [2,12,13]. A minimum is observed near 210 °C on Pd/Al_2O_3 (see Fig. 3). Below that temperature, a maximum arises at 105 °C corresponding to 92% NO conversion predominantly into N_2O, the selectivity for the production of N_2 being equal to 16.5% at the maximum NO conversion. Above 210 °C, the conversion of NO increases again, N_2 being the main N-containing product. Such trends are also observed on Pt/Al_2O_3 in Fig. 4, the conversion of NO by reaction with H_2 starting at lower temperature ~50 °C. These two ranges of conversion could reflect changes in reaction pathways as earlier suggested in the literature [12]. The direct reduction of NO by H_2 could be favoured at low temperature, whereas in situ generated NO_2 could react with H_2 at higher temperature. The formation of nitrates and nitrites species on noble metals or on the support could also occur, these species may further react with H_2. In fact, Machida et al. [14] suggested that subsequent improvements in the selectivity of noble metals could be closely related to the formation of

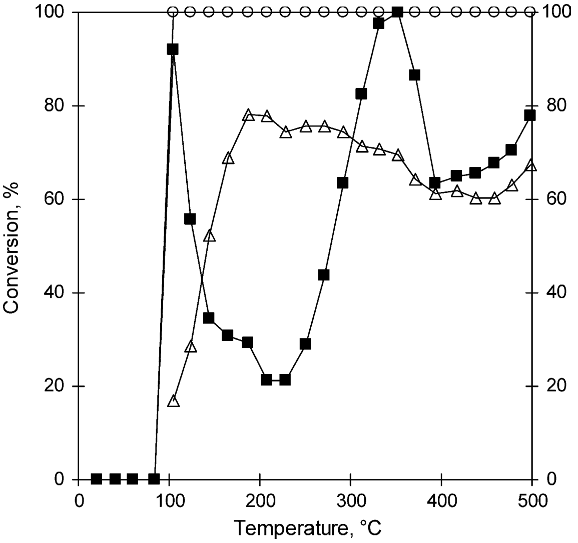

Fig. 3. Temperature-programmed NO + H_2 reaction on Pd/Al_2O_3, pre-reduced in H_2 at 500 °C: NO conversion (■), H_2 conversion (○) and selectivity of N_2 (△); experimental conditions: 0.15 vol.% NO, 0.5 vol.% H_2 and 3 vol.% O_2.

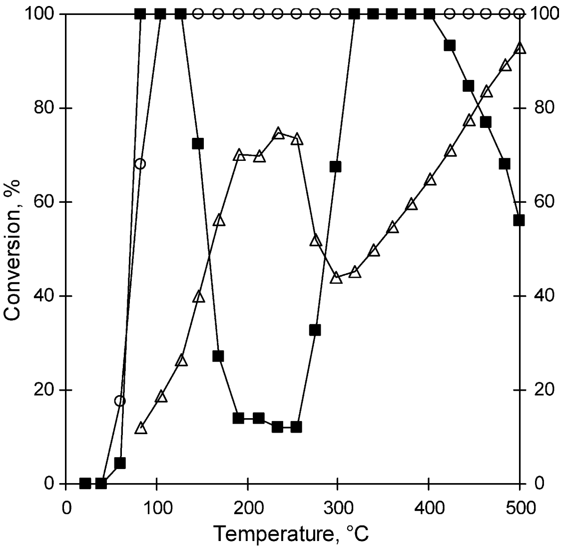

Fig. 4. Temperature-programmed NO + H_2 reaction on Pt/Al_2O_3 pre-reduced in H_2 at 500 °C: NO conversion (■), H_2 conversion (○) and selectivity of N_2 (△); experimental conditions: 0.15 vol.% NO, 0.5 vol.% H_2 and 3 vol.% O_2.

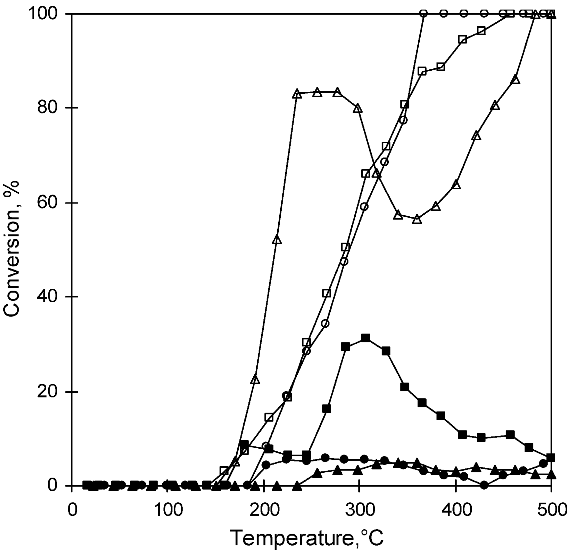

Fig. 5. Temperature-programmed NO + H_2 reaction on $LaCoO_3$ calcined at 500 °C: NO conversion (■), H_2 conversion (□); after reduction at 250 °C: NO conversion (●), H_2 conversion (○); after reduction at 500 °C: NO conversion (▲), H_2 conversion (△); experimental conditions: 0.15 vol.% NO, 0.5 vol.% H_2 and 3 vol.% O_2.

chemisorbed nitrates on Pt and Pd surface and/or on alumina via spill-over process that could explain the high temperature conversion range and the better selectivity towards the production of N_2 than that observed at low temperature either on Pd/Al_2O_3 or on Pt/Al_2O_3. Alternately, the low and high temperature reduction ranges could reflect changes in the oxidation state of noble metals shifting from a reduced to an oxidised state with a rise in temperature. However, both explanations can be reconciled based on the arguments developed by Burch et al. [15,16]. Presumably, Pd catalysts are oxidised under reaction conditions mainly and high temperature and might only convert NO into NO_2.

Fig. 5 shows that $LaCoO_3$ is much less active than noble metals in the reduction of NO by H_2, the extent of conversion depending on the reductive or oxidative pre-treatment. As observed a pre-reduction in H_2 at 500 °C drastically alters NO conversion, the competition being much more in favour of the oxidation of H_2 by O_2. An extensive reduction of $LaCoO_3$ into La_2O_3 and undetectable Co species during the pre-activation treatment in H_2 at 500 °C for 12 h, earlier evidenced by XRD and thermogravimetric analysis [17], are probably related to such a deactivation.

3.2.2. Catalytic properties of supported noble metals on $LaCoO_3$ (with M = Pd or Pt)

3.2.2.1. Influence of the thermal pre-treatment of M/$LaCoO_3$. Temperature conversion and selectivity curves recorded on $Pd/LaCoO_3$ and $Pt/LaCoO_3$ are reported in Figs. 6 and 7, respectively. Particular attention has been paid to the thermal activation treatment on the overall NO conversion and the selectivity for the production of N_2. As illustrated in Fig. 6, the extent of reduction greatly influences the catalytic performances of $Pd/LaCoO_3$. Clearly, pre-reduction in H_2 at 500 °C improves the low temperature NO conversion range and significantly enhances the selectivity towards the production of N_2 compared to Pd/Al_2O_3. On the other hand, the high temperature NO conversion range is attenuated. Now, regarding the influence of the pre-activation thermal treatment, the catalytic performances of $Pd/LaCoO_3$ are low after calcination in air and further reduction in H_2 at 250 °C with a strong attenuation of the low temperature NO conversion range. It is worthwhile to note that the conversion starts only at 200 °C on the calcined $Pd/LaCoO_3$ sample and remains below 20% NO conversion in the whole range of temperature. The beneficial effect of the reduction in H_2 is also noticeable of $Pt/LaCoO_3$ but in that case the most prominent observation is the disappearance of the high conversion range. Both tendencies agree with the fact that metallic noble metal sites, particularly Pd, in interaction with $LaCoO_3$ benefits the low temperature conversion compared to a classical γ-alumina support, while oxidic Pt and Pd species favour the competitive oxidation of hydrogen by O_2. Such changes in the catalytic behaviour of noble metals could be explained by a bi-functional mechanism involving anionic vacancies from the support and metallic noble metal sites according to previous discussions [11]. Alternately, the nature of interactions with the support material could also change the adsorption properties of noble metals. By way of illustration, previous findings obtained during the reaction of NO by hydrogen on Pd/Al_2O_3–La_2O_3 show that the formation of Pd_3La alloy during the activation thermal treatment under reductive atmosphere between 400 and 700 °C enhances the catalytic activity [18].

The peculiar properties of pre-reduced supported Pd catalyst on $LaCoO_3$ activated in H_2 at 500 °C could be

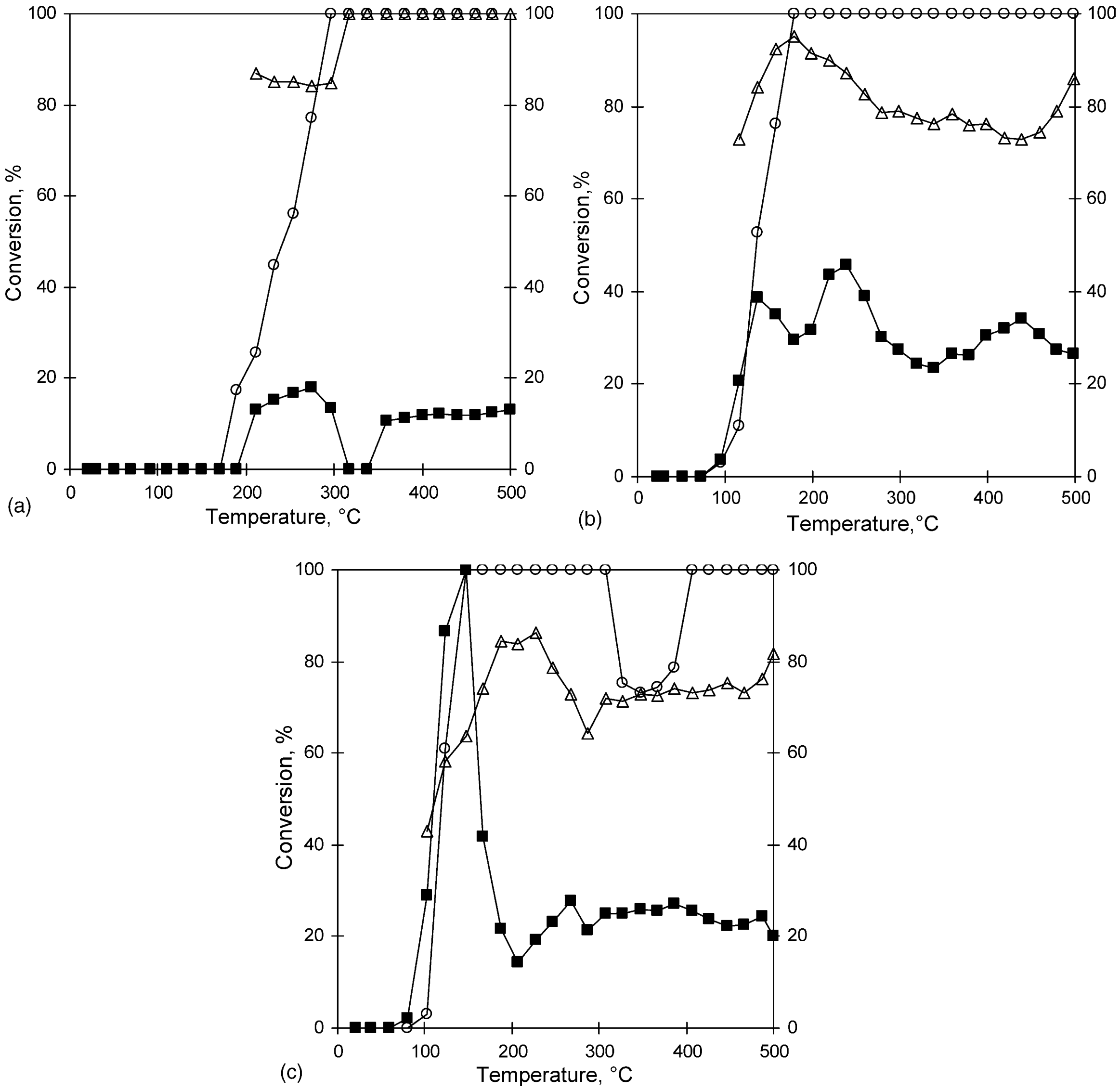

Fig. 6. Temperature-programmed NO + H_2 reaction on Pd/$LaCoO_3$ calcined at 500 °C (a), after subsequent reduction in H_2 at 250 °C (b) and after reduction at 500 °C (c): NO conversion (■), H_2 conversion (○) and selectivity of N_2 (△); experimental conditions: 0.15 vol.% NO, 0.5 vol.% H_2 and 3 vol.% O_2.

related to the nature of the interaction between Pd and La generated during the bulk reduction of $LaCoO_3$ into La_2O_3 and well-dispersed Co species. Alternately, the formation of bimetallic particles Pd–Co may also originate changes in the intrinsic adsorption properties of noble metals.

3.2.2.2. Influence of water on the catalytic performances. Figs. 8 and 9 illustrate the influence of water on the selectivity and on the overall conversion of NO. Obviously, water inhibits the conversion at high temperature whatever the catalyst composition. Such a tendency could easily be explained by the stabilisation of strongly chemisorbed nitrates either on alumina or $LaCoO_3$ in the presence of water, as previously reported in the literature [19,20]. On the other hand, no clear tendency arises from the examination of the effect of water on the catalytic performances of supported Pd and Pt catalyst at low temperature. As a matter of fact divergences are observable according to the nature of the noble metal. Further comparisons of NO conversion curves recorded in the presence (Fig. 8(b)) or absence (Fig. 6(c)) of water show that H_2O promotes the activity in the conversion of NO by reaction with H_2 on Pd/$LaCoO_3$, while an inhibiting effect of water on the NO conversion prevails on Pd/Al_2O_3. Interestingly, reverse trends are observed on Pt, since NO conversion starts at lower temperature on Pt/Al_2O_3 in the presence of water, whereas no significant effect seems to occur on Pt/$LaCoO_3$. It is worthwhile to note that, at low temperature, H_2O has a detrimental effect on the selectivity behaviour of Pd/Al_2O_3, NO being quasi-completely converted into N_2O. On the other hand, the selectivity of Pd/$LaCoO_3$ is not significantly affected in the presence of water.

The usual beneficial effect of water on the conversion is usually supposed to be due to the dissociation of H_2O over noble metals that generates an increase in the coverage of

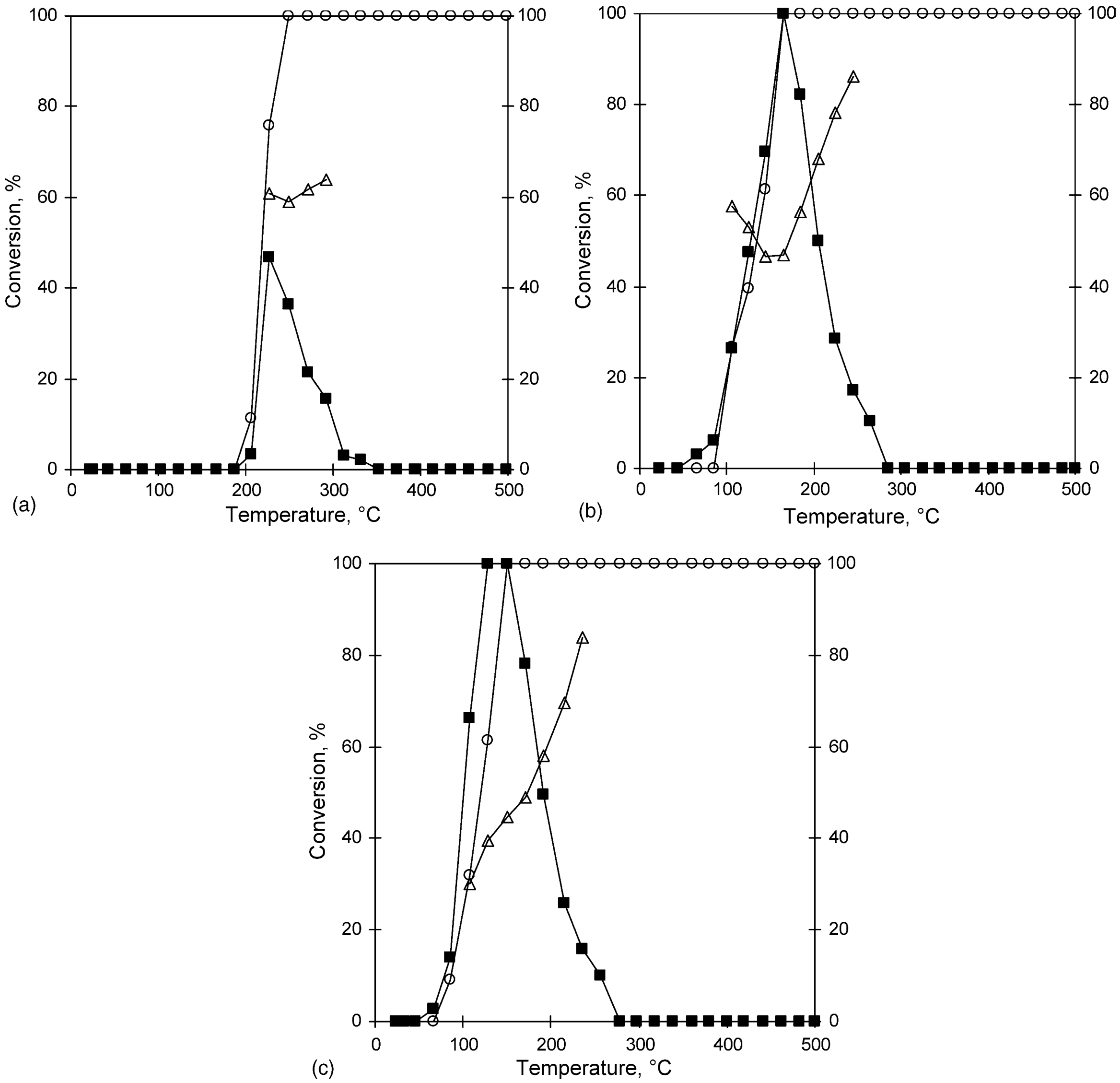

Fig. 7. Temperature-programmed NO + H_2 reaction on Pt/$LaCoO_3$ calcined at 500 °C (a), after a subsequent reduction in H_2 at 250 °C (b) and after reduction at 500 °C (c): NO conversion (■), H_2 conversion (○) and selectivity of N_2 (△); experimental conditions: 0.15 vol.% NO, 0.5 vol.% H_2 and 3 vol.% O_2.

chemisorbed hydrogen atoms. Such dissociation involves metallic sites. Frequently, the presence of strongly chemisorbed O atoms on the surface requires high temperature desorption either on Pd(1 0 0) [21] or Pt(1 1 1) [22]. Previous investigations have shown that the hydrogen coverage is a significant parameter for controlling the activity and the selectivity for the transformation of NO into N_2. As a matter of fact, previous authors who investigated the kinetics of the NO + H_2 reaction on Rh based catalysts suggested that chemisorbed H atoms could assist the dissociation of NO which is usually considered as rate determining step [23]. Consequently, the difference observed at low temperature between Pd and Pt, mainly on alumina could be explained by different oxygen coverage and/or by an extensive segregation of oxidic palladium species that could suppress the dissociation of H_2O on Pd/Al_2O_3. On the other hand, the beneficial effect of water observed on Pd/$LaCoO_3$ could be related to the peculiar interaction with the support which preserves the metallic character of Pd more oxidisable than Pt.

At higher temperature, the stabilisation of more strongly chemisorbed nitrates and nitrites species in the presence of water [19] and/or a partial oxidation of noble metal could partially or completely suppress the high temperature activity in the conversion of NO [14], the oxidation of H_2 by O_2 occurring predominantly.

4. Conclusion

Generally speaking, hydrogen is usually recognised as none selective for reducing NO_x under lean conditions. Our results show a remarkable behaviour at low temperature between 50 and 200 °C, the reduction of NO by H_2 being

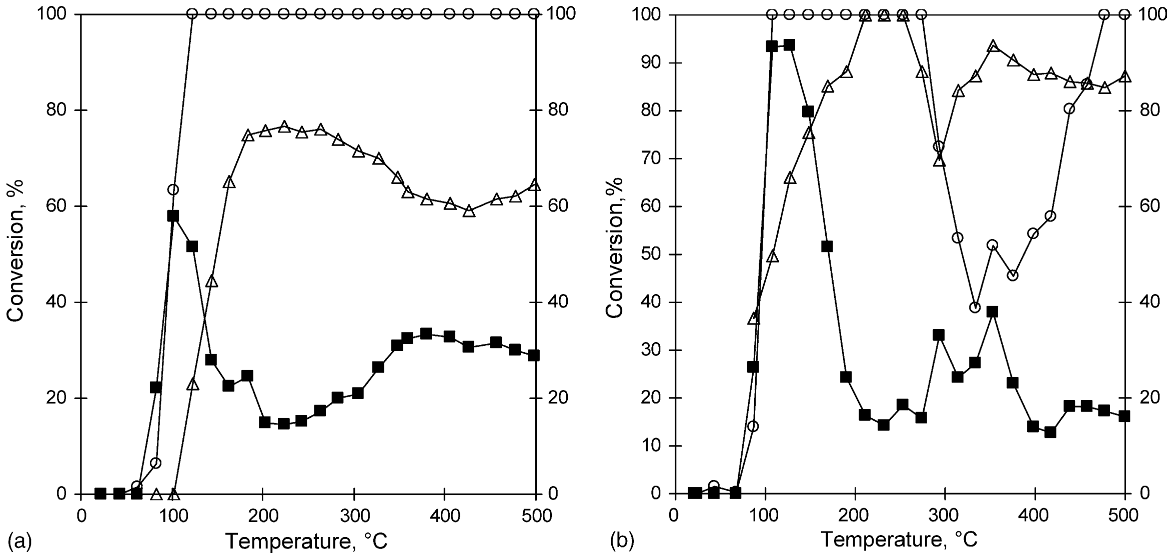

Fig. 8. Influence of water on the catalytic performances of Pd/Al_2O_3 (a) and $Pd/LaCoO_3$ (b) pre-reduced in H_2 at 500 °C: NO conversion (■), H_2 conversion (○) and selectivity of N_2 (△); experimental conditions: 0.15 vol.% NO, 0.5 vol.% H_2, 3 vol.% O_2 and 5 vol.% H_2O.

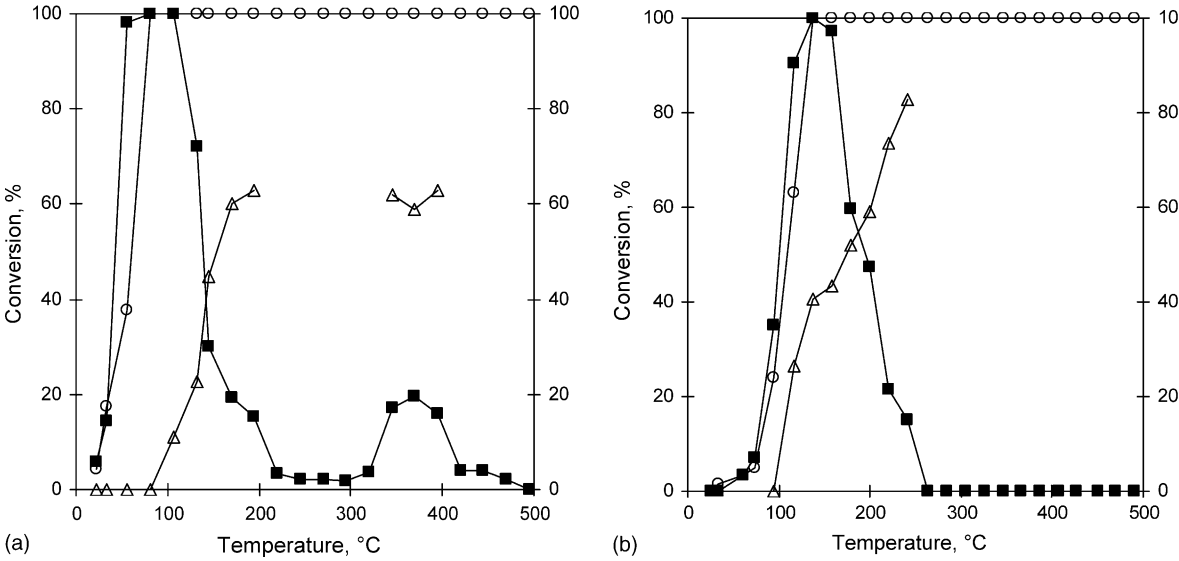

Fig. 9. Influence of water on the catalytic performances of Pt/Al_2O_3 (a) and $Pt/LaCoO_3$ (b) pre-reduced in H_2 at 500 °C: NO conversion (■), H_2 conversion (○) and selectivity of N_2 (△); experimental conditions: 0.15 vol.% NO, 0.5 vol.% H_2, 3 vol.% O_2 and 5 vol.% H_2O.

much more favoured than the oxidation of H_2 by O_2 in this temperature range. In fact, it has been found that the catalytic reduction of NO by H_2 under lean conditions is strongly influenced by the nature of the support material and the pre-activation thermal treatment prior to reaction under oxidising or reducing atmosphere, especially when water is added to the reaction mixture. Two conversion ranges have been observed that could be explained by the occurrence of different reaction pathways. At low temperature, the direct $NO + H_2$ reaction would involve metallic Pt and Pd sites, whereas oxidic platinum and palladium species would mainly favour the competitive oxidation of H_2 by O_2. At high temperature, the $NO_2 + H_2$ reaction and/or the involvement of nitrites and nitrates species could be involved. Further stabilisation of such species in the presence of water would suppress the NO conversion. But the most significant result is obtained on the low conversion range particularly on $LaCoO_3$. The interaction between Pd and $LaCoO_3$ probably stabilises the metallic character of Pd that could be essential to observe a promotional effect of water on the conversion and the selectivity.

Acknowledgments

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References

[1] A. Barrera, M. Viniegra, P. Bosch, V.H. Lara, S. Fuentes, Appl. Catal. B 34 (2001) 97.
[2] T. Namba, C. Kohno, S. Masukawa, J. Uchisawa, N. Nakayama, A. Obuchi, Appl. Catal. B 46 (2003) 353.
[3] C.N. Costa, P.G. Savva, C. Andronikou, P.S. Lambrou, K. Polychonopoulou, V.C. Belessi, V.N. Stathopoulos, P.J. Pomonis, A.M. Efstathiou, J. Catal. 209 (2002) 456.
[4] J.-B. Yang, O.-Z. Fu, D.-Y. Wu, S.-D. Wang, Appl. Catal. B 49 (2004) 61.
[5] M.S.G. Baythour, F.R. Sale, J. Mater. Sci. 17 (1982) 2757.
[6] L. Simonot, F. Garin, G. Maire, Appl. Catal. 11 (1997) 167.
[7] A. Lindstedt, D. Stromberg, M. Abul Milh, Appl. Catal. A 116 (1994) 109.
[8] G. Tejuca, J.-L. Fierro, J.M.D. Tascon, Adv. Catal. 36 (1989) 237.
[9] L.B. Sis, G.P. Wirtz, S.C. Sorenson, J. Appl. Phys. 44 (1973) 5553.
[10] M.A. Pena, J.L. Fierro, Chem. Rev. 101 (2001) 198.
[11] D. Ferri, L. Forni, M.A.P. Dekkers, B.E. Nieuwenhuys, Appl. Catal. B 16 (1998) 339.
[12] A. Ueda, T. Nakao, M. Azuma, T. Kobayashi, Catal. Today 45 (1998) 135.
[13] C.N. Costa, V.N. Stathapoulos, V.C. Belessi, A.M. Efstathiou, J. Catal. 197 (2001) 350.
[14] M. Machida, S. Ikeda, D. Kuragi, T. Kijima, Appl. Catal. B 35 (2001) 107.
[15] R. Burch, M.D. Coleman, Appl. Catal. B 23 (1999) 115.
[16] R. Burch, P.K. Loader, N.A. Cruise, Appl. Catal. A 147 (1996) 45.
[17] M. Pirez-Engelmann, P. Granger, L. Leclercq, G. Leclercq, Top. Catal. 30–31 (2004) 59.
[18] A. Barrera, M. Viniegra, P. Bosch, V.H. Lara, S. Fuentes, Appl. Catal. B 34 (2001) 97.
[19] S. Kikuyama, I. Matsukuma, R. Hikuchi, K. Sasaki, K. Eguchi, Appl. Catal. A 5840 (2001) 1.
[20] S. Hodjati, K. Vaezzadeh, C. Petit, V. Pitchon, A. Kienneman, Appl. Catal. B 26 (1996) 420.
[21] E.M. Stuve, S.W. Jorgensen, R.J. Madix, Surf. Sci. 146 (1984) 179.
[22] J.R. Creighton, J.M. White, Surf. Sci. 122 (1982) 648.
[23] W. Hecker, A.T. Bell, J. Catal. 92 (1985) 247.