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Kinetic investigation of the NO reduction by H_2 over noble metal based catalysts

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Abstract

This paper reports a kinetic investigation of the overall reduction of NO by H_2 over supported palladium based catalysts. Drastic changes in the kinetic features of Pd were found after deposition on reducible $LaCoO_3$ materials in comparison with alumina. Peculiar interactions between palladium and $LaCoO_3$ build up during a pre-activation thermal treatment in H_2 at high temperature which completely modify the kinetic behaviour of Pd. In such a case, a classical Langmuir–Hinshelwood mechanism, previously proposed on Pd/Al_2O_3, is unable to model steady-state rate measurements on pre-reduced $Pd/LaCoO_3$. A bi-functional mechanism involving anionic vacancies at the vicinity of palladium particles leads to a better agreement.

Keywords: Pd based catalysts; $NO + H_2$ reaction; Hydrogen; N_2O selectivity; Reaction mechanism

1. Introduction

Presently, a growing interest regarding the use of hydrogen in environmental catalysis is discernible [1–7]. In the particular case of NO_x abatement processes for mobile and stationary sources, hydrogen is potentially more attractive than ammonia for low-temperature exhaust gases in spite of its low selectivity under lean conditions. Previous investigations also reported a poor selectivity towards the transformation of NO into nitrogen in those running conditions [4] due to the parallel formation of N_2O and ammonia according to reactions (2) and (3):

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O \quad (1)$$

$$2NO + H_2 \rightarrow N_2O + H_2O \quad (2)$$

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \quad (3)$$

However, recent studies [2,5–7] have shown that the production of nitrogen can be considerably enhanced when noble metals are supported over reducible materials exhibiting a perovskite structure. Now, a better understanding of the reaction mechanisms and a better definition of the active sites are prerequisite steps for optimising the catalytic performances of noble metals supported over those materials, particularly Pd [5,8]. Subsequent changes in their intrinsic properties probably depend on the extent of interaction between noble metal particles and the support. Previous mechanistic investigations of the $NO + H_2$ reaction on Rh/SiO_2 suggested a Langmuir–Hinshelwood mechanism [9,10]. Recently, It was also found in our laboratory that this mechanism (see Fig. 1) prevails on Pd/Al_2O_3 [11], involving a dissociation step of chemisorbed NO molecules assisted by chemisorbed hydrogen atoms (step (6)). The selectivity towards the production of N_2O (S_{N_2O}) weakly depends on the partial pressures of the reactants (H_2 and NO). Such weak partial pressure dependencies of S_{N_2O} have been earlier observed and discussed on Rh/Al_2O_3 during the $CO + NO$ reaction [12]. Such a tendency is observed when NO strongly adsorbs at the surface. It was found that the competition between adsorbates both on Rh and on Pd is largely in favour of NO. Consequently, in our experimental conditions, Pd is predominantly covered by chemisorbed NO molecules in the course of the $NO + H_2$ reaction [11], the production of nitrogen mainly involving step (8) at the expense of step (7)

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Langmuir-Hinshelwood Mechanism 1		*Bi-functional mechanism 2*	
(4)	$NO + \ast \Leftrightarrow NO_{ads}$	(4)	$NO + \ast \Leftrightarrow NO_{ads}$
(5)	$H_2 + 2\ast \Leftrightarrow 2H_{ads}$	(5')	$H_2 + \ast \Leftrightarrow H_{2,ads}$
(6)	$NO_{ads} + H_{ads} \rightarrow N_{ads} + OH_{ads}$	(15)	$\text{'O'} + H_{2,ads} \rightarrow \text{'V'} + H_2O + \ast$
(7)	$N_{ads} + N_{ads} \rightarrow N_2 + 2\ast$	(16)	$NO_{ads} + \text{'V'} \rightarrow \text{'O'} + N_{ads}$
(8)	$NO_{ads} + N_{ads} \rightarrow N_2 + O_{ads} + \ast$	(8)	$NO_{ads} + N_{ads} \rightarrow N_2 + O_{ads} + \ast$
(9)	$NO_{ads} + N_{ads} \rightarrow N_2O + 2\ast$	(9)	$NO_{ads} + N_{ads} \rightarrow N_2O + 2\ast$
(10)	$N_{ads} + H_{ads} \rightarrow NH_{ads} + \ast$	(17)	$N_{ads} + H_{2,ads} \rightarrow NH_{ads} + H_{ads}$
(11)	$NH_{ads} + H_{ads} \rightarrow NH_{2,ads} + \ast$	(18)	$NH_{ads} + H_{2,ads} \rightarrow NH_{2,ads} + H_{ads}$
(12)	$NH_{2,ads} + H_{ads} \rightarrow NH_3 + 2\ast$	(19)	$NH_{2,ads} + H_{2,ads} \rightarrow NH_3 + H_{ads} + \ast$
(13)	$O_{ads} + H_{ads} \rightarrow OH_{ads} + \ast$	(20)	$O_{ads} + H_{2,ads} \rightarrow H_2O + 2\ast$
(14)	$OH_{ads} + H_{ads} \rightarrow H_2O + 2\ast$	(13)	$O_{ads} + H_{ads} \rightarrow OH_{ads} + \ast$
		(14)	$OH_{ads} + H_{ads} \rightarrow H_2O + 2\ast$

Fig. 1. Reaction mechanisms over noble metal based catalysts. * stands for a vacant metallic site. "O" is an oxygen species, "V" being an anionic vacancy from the support.

corresponding to the recombination of two adjacent chemisorbed nitrogen atoms.

This study highlights the peculiar kinetic properties of Pd/$LaCoO_3$ which cannot be depicted by a conventional Langmuir–Hinshelwood mechanism. An alternative bi-functional mechanism involving anionic vacancies at the vicinity of palladium particles has been considered.

2. Experimental

2.1. Catalyst preparation and characterisation

The preparation procedure of $LaCoO_3$ ($20\ m^2\ g^{-1}$) was described elsewhere [13,14] using a *so-called* sol–gel method involving a citrate route. Supported palladium catalysts on $LaCoO_3$ were prepared according to a classical wet impregnation route using palladium nitrate solutions with adjusted concentrations in order to obtain 1 wt.% Pd. The impregnated samples were calcined in air at 400 °C and then reduced at 450 °C in pure H_2 overnight. In these reductive conditions, an extensive reduction of PdO and $LaCoO_3$ into metallic palladium and cobalt particles on La_2O_3 occurred [14]. The hydrogen uptake, calculated from H_2 chemisorption measurements performed at 100 °C on pre-reduced samples in H_2 at 450 °C, was 40.4 and 7.5 μmol per gram of catalyst, respectively on Pd/Al_2O_3 and Pd/$LaCoO_3$ which corresponded with Pd dispersion of approximately 0.86 and 0.16. However, The accuracy on the Pd dispersion could be poor because previous investigations [8,15] revealed the involvement of hydrogen spill-over effects during H_2 chemisorption measurements particularly when Pd is dispersed on reducible materials. Previous investigations dealing with this aspect on Pd supported on ceria–zirconia mixed oxides have shown that H_2 spill-over strongly depended on the pre-reductive thermal treatment in H_2, the intensity of these hydrogen transfer phenomena decreasing with an increasing reduction temperature [15]. It was expected that this process should not operate significantly in our operating conditions. However it cannot be strictly ruled out. Additional experiments on reduced $LaCoO_3$ support did not show a significant hydrogen uptake (below 0.1 μmol per gram of catalyst).

2.2. Catalytic testing

Catalytic measurements were performed in differential conditions in a fixed bed flow reactor running at atmospheric pressure. The catalytic set up was described elsewhere [16]. The catalyst was in a powder form with an average grain size of 80 μm. The gaseous mixture was analysed by a *Balzer* mass spectrometer and a *Hewlett Packart 5890 series II* chromatograph fitted with a thermal conductivity detector. Reactants and products were separated on a *CTR1* column supplied by *Alltech*. Typically, catalytic testings were performed with 0.1 g of catalyst, diluted with 0.2 g of α-Al_2O_3, and a global flow rate of $10\ L\ h^{-1}$. The space velocities were equal to 50,000 and $28{,}000\ h^{-1}$, respectively on Pd/Al_2O_3 and Pd/$LaCoO_3$. Prior to reaction, the catalyst samples were *in situ* reduced in hydrogen at 450 °C.

3. Results

3.1. Temperature dependency of the rate

Steady-state rate measurements on Pd/$LaCoO_3$ were performed in stoichiometric conditions with inlet partial pressures of NO and H_2 of 1×10^{-2} atm in the temperature range 90–130 °C. The apparent activation energy, relative to the

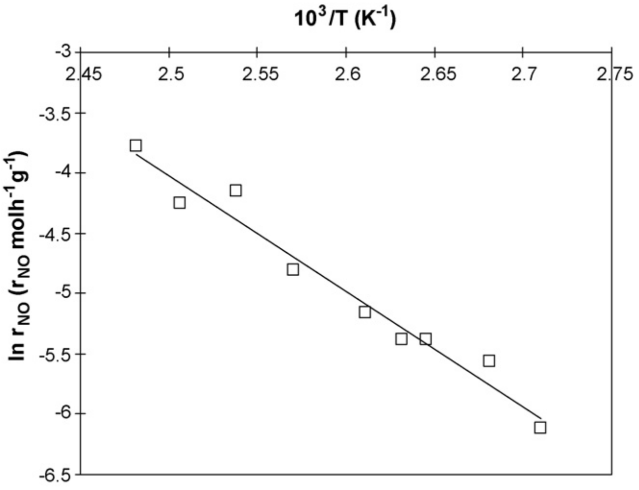

Fig. 2. Arrhenius plot for the NO + H_2 reaction on Pd/$LaCoO_3$, pre-activated in H_2 at 450 °C, under stoichiometric conditions with inlet partial pressures of H_2 and NO of 1×10^{-2} atm: (—) predicted plot calculated according to $r_{NO} = r_2$; (□) experimental plot.

overall conversion of NO, calculated from the slope of the Arrhenius plot in Fig. 2 is equal to 79.7 kJ mol^{-1}. This value slightly differs from that previously obtained on Pd/Al_2O_3 equal to 68.1 kJ mol^{-1}.

3.2. *Influence of partial pressures of the reactants*

The partial pressure dependencies of the rate of NO conversion on Pd/$LaCoO_3$ were investigated at 110 °C in the partial pressure ranges (1.3–14.4) $\times 10^{-3}$ and (4.6–13.4) $\times 10^{-3}$ atm for NO and H_2, respectively. The apparent reaction orders with respect to the partial pressure of H_2 and NO, calculated from regression analysis using kinetic data reported in Figs. 3 and 4, are respectively equal to 1 and −0.7. The negative value obtained for NO highlights a strong inhibiting effect on the reaction rate, as earlier evidenced [11,17], which suggests that metallic sites are predominantly covered by chemisorbed NO molecules. Pd/$LaCoO_3$ exhibits a similar selectivity behaviour than Pd/Al_2O_3 [11], the selectivity for the production of N_2O (S_{N_2O}) being constant, equal to 0.60 ± 0.02, irrespective of the partial pressure conditions.

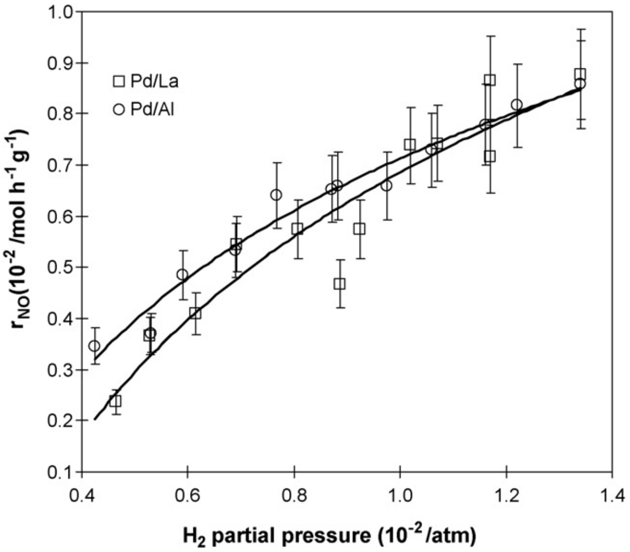

Fig. 3. Hydrogen partial pressure dependency of the rate of NO conversion on pre-activated Pd/$LaCoO_3$ in H_2 at 450 °C – reaction temperature = 110 °C – inlet NO partial pressure 1×10^{-2} atm.

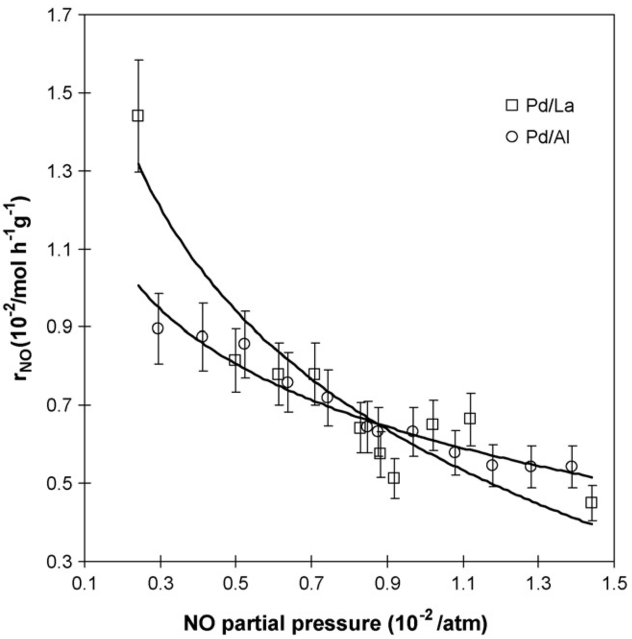

Fig. 4. NO partial pressure dependency of the rate of NO conversion on pre-activated Pd/$LaCoO_3$ in H_2 at 450 °C – reaction temperature = 110 °C – inlet H_2 partial pressure 1×10^{-2} atm.

4. Discussion

Kinetic data obtained for the NO + H_2 reaction on Pd/$LaCoO_3$ differ from those previously obtained on Pd/Al_2O_3 [11] and on Rh [9]. Regarding this latter investigation, Hecker and Bell modelled their rate measurements on Rh/SiO_2 according to mechanism 1. A steady-state rate equation, given by Eq. (20), can be established according to the overall transformation of NO (Eqs. (1)–(3)). The subsequent Eq. (21) can be derived from mechanism 1 by neglecting step (7), in accordance with the weak partial pressure dependencies of S_{N_2O} on Pd/$LaCoO_3$, by assuming adsorptions of the reactants at equilibrium and a surface predominantly covered by chemisorbed NO molecules [11]:

$$r_{NO} = 2(r_{N_2} + r_{N_2O}) + r_{NH_3} \tag{20}$$

$$r_{NO} = r_1 = \frac{2k_6\lambda_{NO}P_{NO}\sqrt{\lambda_H P_{H_2}}}{(1 + \lambda_{NO}P_{NO} + \sqrt{\lambda_H P_{H_2}})^2} \tag{21}$$

Hecker and Bell [9] also showed that the oxidation state of Rh may influence the kinetic behaviour, lower activation energies being obtained on pre-oxidised samples. In our case, the first order with respect to the partial pressure of H_2 on Pd/$LaCoO_3$ may reflect a reaction limited by the adsorption of H_2 according to mechanism 1, or by a dissociation step of NO assisted by molecular hydrogen species on Pd according to the following reaction sequence [11]:

$$H_2 + * \Leftrightarrow H_{2,ads}$$

$$NO_{ads} + H_{2,ads} \rightarrow NH_{ads} + OH_{ads} \tag{22}$$

Accordingly, Eq. (23) can be established:

$$r_{NO} = r'_1 = \frac{2k_{22}\lambda_{NO}P_{NO}\lambda_H P_{H_2}}{(1 + \lambda_{NO}P_{NO} + \lambda_H P_{H_2})^2} \tag{23}$$

The former assumption was previously invalidated on Pd/$LaCoO_3$ whereas the involvement of step (22) correctly modelled rate measurements on Pd/$LaCoO_3$ only after pre-activation in H_2 in mild conditions at 250 °C [11]. Such a situation could occur on NO saturated surfaces where the probability of finding two adjacent sites for the dissociative adsorption of hydrogen would be very low. Such an explanation is partly supported by recent experiments of H_2 adsorption on Pd(1 1 1) of Mitsui et al. [18] who found that at high surface coverage the classical Langmuir picture of second order adsorption kinetics requiring pairs of empty sites for the dissociative chemisorption is too simplistic, H_2 adsorption requiring ensemble of three or more H-free nearest neighbour fcc sites. More recently, Lopez et al. [19] investigated the kinetics of hydrogen adsorption on a precovered Pd(1 1 1) surface and led to similar conclusions. DFT calculations provided energy profiles which evidenced a physisorbed molecular state. In accordance with these previous investigations, hydrogen could remain adsorbed as a precursor molecular species on Pd predominantly covered by NO. Previous investigations on the kinetics of the reaction on Pd/$LaCoO_3$, reduced in mild conditions, showed a good fit with Eq. (23) based on a bimolecular reaction between chemisorbed NO and H_2 molecules [11]. However, some discrepancies arise on a pre-reduced catalyst in H_2 at 450 °C. As previously mentioned an extensive reduction of $LaCoO_3$ operates in those conditions. Recent investigations of the NO + H_2 reaction on Pd/Al_2O_3–La_2O_3 [20,21] suggest the formation of Pd_3La alloy during a thermal treatment in H_2 between 400 and 700 °C which could be responsible of the selectivity enhancement towards the production of N_2. In fact, different arguments could be proposed for explaining such changes in catalytic properties. The interactions between the metal and the support may change the adsorption properties of Pd and the rate constants associated with steps on the metal according to mechanism 1. Alternatively, changes in the catalytic behaviour could be related to the creation of different active sites localised at the interface metal/support where Pd and anionic vacancies from the support could co-operate. Consequently, an alternative bi-functional mechanism (mechanism 2 in Fig. 1) could be considered for the kinetics of the NO + H_2 reaction on Pd supported on $LaCoO_3$ extensively reduced into La_2O_3 and CoO_x. Eqs. (24)–(27) can be easily derived from mechanism 2 based on previous assumptions:

$$r_{NO} = r_2 = 2k_{16}\theta^*_{NO}\theta_V \tag{24}$$

where $\theta_V = 1 - \theta_O$ denotes the fraction of surface anionic vacancies, θ_O corresponding to the surface oxygen species from the support. θ^*_{NO} stands for the NO coverage on Pd particles. By applying the steady-state approximation to anionic vacancies from the support 'V', Eq. (25) can be obtained:

$$\theta_V = \frac{k_{15}\theta^*_{H_2}}{k_{16}\theta^*_{NO} + k_{15}\theta^*_{H_2}} \tag{25}$$

with

$$\theta^*_{NO} = \frac{\lambda_{NO}P_{NO}}{1 + \lambda_{NO}P_{NO} + \lambda_H P_{H_2}} \tag{26}$$

and

$$\theta^*_{H_2} = \frac{\lambda_H P_{H_2}}{1 + \lambda_{NO}P_{NO} + \lambda_H P_{H_2}} \tag{27}$$

according to a molecular adsorption of H_2 via step (5′).

In fact, in the foregoing discussion it was assumed the existence of various mechanisms which are sometimes difficult to unambiguously discriminate. It seems obvious that the support materials may exhibit different behaviour as a consequence either of changes in the electronic or structural properties of the Pd particles or of the participation of anionic vacancies from the reduced support at the metal/support interface. Based on these considerations a mono-functional mechanism (mechanism 1 in Fig. 1 accounting for step (22) for the dissociation of NO_{ads} species) or a bi-functional one (mechanism 2) may be equally considered for modelling our rate measurements on Pd. Consequently, the rate of the overall NO transformation on pre-activated Pd/$LaCoO_3$ in H_2 at 450 °C can be given by Eq. (28):

$$r_{NO} = r'_1 + r_2 = \frac{2k_{22}\lambda_{NO}P_{NO}\lambda_H P_{H_2}}{(1 + \lambda_{NO}P_{NO} + \lambda_H P_{H_2})^2} + \frac{2k_{16}k_{15}\lambda_{NO}P_{NO}\lambda_H P_{H_2}}{(k_{16}\lambda_{NO}P_{NO} + k_{15}\lambda_H P_{H_2})(1 + \lambda_{NO}P_{NO} + \lambda_H P_{H_2})} \tag{28}$$

Such a rate equation cannot be linearised and then solved using a graphic method. An optimisation method, earlier described [12], was implemented using a non-linear regression analysis for adjusting the rate constants k_n and the equilibrium

Table 1
Optimised kinetic and thermodynamic parameters calculated at 110 °C for the NO + H_2 reaction on supported palladium catalysts

Catalyst	Rate equation	k_6[a]	k_{22}	k_{15}[a]	k_{16}[a]	λ_{NO} (atm^{-1})	λ_H (atm^{-1})
Pd/Al_2O_3[b]	(21)	1.08 ± 0.32		–	–	48.8 ± 7.3	$(5.5 \pm 0.8) \times 10^{-2}$
Pd/$LaCoO_3$	(28)		≅0	$(3.3 \pm 0.5) \times 10^{-2}$	0.32 ± 0.05	500 ± 75	60 ± 9

[a] mol h^{-1} g^{-1}.

[b] Calculated from data in Ref. [11].

Table 2
Temperature dependency of the intrinsic rate constant for NO dissociation and of the equilibrium adsorption constants of NO and H_2 on supported palladium catalysts

Catalyst	A_6[a]	A_{15}[a]	A_{16}[a]	E_6[b]	E_{15}[b]	E_{16}[b]	f_{NO} (10^{-5} atm^{-1})	f_H (10^{-4} atm^{-1})	$\Delta H_{ads,NO}$[b]	$\Delta H_{ads,H}$[b]
Pd/Al_2O_3	970 ± 110			75 ± 8			7.2 ± 0.8	3.5 ± 0.4	−42.6 ± 5.0	−16.6 ± 2.0
$Pd/LaCoO_3$		5.1 ± 0.8	7.0 ± 1.1		75 ± 12	70 ± 11	3.6 ± 0.5	3.5 ± 0.5	−49.0 ± 7.3	−29.1 ± 4.3

[a] 10^8 mol h^{-1} g^{-1}.
[b] kJ mol^{-1}.

adsorption constants of NO and of hydrogen (λ_{NO} and λ_H). The adjustment routine has been achieved using the solver set up on Excel 6 from *Microsoft*. It consists in minimising the square difference between experimental rates and those calculated from Eq. (28). The results obtained from the adjustment routine, using the sets of rates in Figs. 3 and 4, are reported in Table 1 and compared with the optimised values previously obtained on Pd/Al_2O_3 [11]. As observed, the rate constant k_{22} related to the dissociation of chemisorbed NO over metallic Pd sites on $Pd/LaCoO_3$ tends towards zero. Consequently, a Langmuir–Hinshelwood mechanism seems to be unlikely for the kinetics of the $NO + H_2$ reaction on $Pd/LaCoO_3$, the bi-functional mechanism reported in Fig. 1 being probably more representative. Consequently, $r_{NO} \cong r_2$ on pre-reduced $Pd/LaCoO_3$ in H_2 at 450 °C.

Now, the temperature dependency of the rate constants k_n and of the equilibrium constants of NO and H_2 can be modelled from rate measurements performed at various temperatures (see Fig. 2). It consists in determining the pre-exponential factors A_n and f_i of the rate constants k_n and of the equilibrium constants λ_i, and the corresponding values for the activation energies E_n and for the adsorption enthalpies of the reactants $\Delta H_{ads,i}$ (with i = NO, H_2) in accordance with the following expressions:

$$k_n = A \exp\left(-\frac{E_n}{RT}\right) \tag{29}$$

$$\lambda_i = f_i \exp\left(-\frac{\Delta H_{ads,i}}{RT}\right) \quad \text{with } f_i = \exp\left(\frac{\Delta S_{ads,i}}{R}\right) \tag{30}$$

where $\Delta S_{ads,i}$ is defined at $P = 1$ atm according to the unit atm^{-1} chosen for the equilibrium adsorption constant λ_i.

The results of the adjustment routine in Table 2 are compared with those previously obtained on Pd/Al_2O_3. As illustrated in Fig. 5 the correlation between predicted and experimental rates shows a good agreement. Various comments arise from the examination of the adjusted kinetic and thermodynamic parameters listed in Table 2. It is interesting to note that the energy of activation corresponding to the refilling step of anionic vacancies (step (16)) is slightly lower than that corresponding to their formation. Such slight differences, which occur within the margin of error, suggest the predominance of a bi-functional mechanism in a wider range of temperature on $LaCoO_3$ than on conventional ceria based three-way catalysts [22]. As previously found on Pt–Rh/Al_2O_3–CeO_2 [22] and on $Pd/Ce_xZr_{1-x}O_2$ [23] an extensive reduction of ceria usually occurs with a rise in temperature which suppresses the synergy effect of ceria on the overall activity in the conversion of NO. Based on these observations, the use of perovskite based catalysts could be potentially interesting for increasing the oxygen storage properties of noble metals. Now, the comparison of the adsorption enthalpies of hydrogen on pre-reduced $Pd/LaCoO_3$ and Pd/Al_2O_3 shows a strengthening of the Pd–H bond on the former catalyst which could be explained by the peculiar interactions between Pd particles and LaO_x species generated during the pre-activation thermal treatment of $Pd/LaCoO_3$ in H_2 at 450 °C. In accordance with previous investigations [20,21], such an interaction could preserve the metallic character of Pd sites. Such behaviour could be a key factor in determining the selectivity of noble metals, previous studies suggesting that the formation of N_2 would mainly involve metallic sites, while the production of N_2O would preferentially occur on oxidised noble metal particles [24].

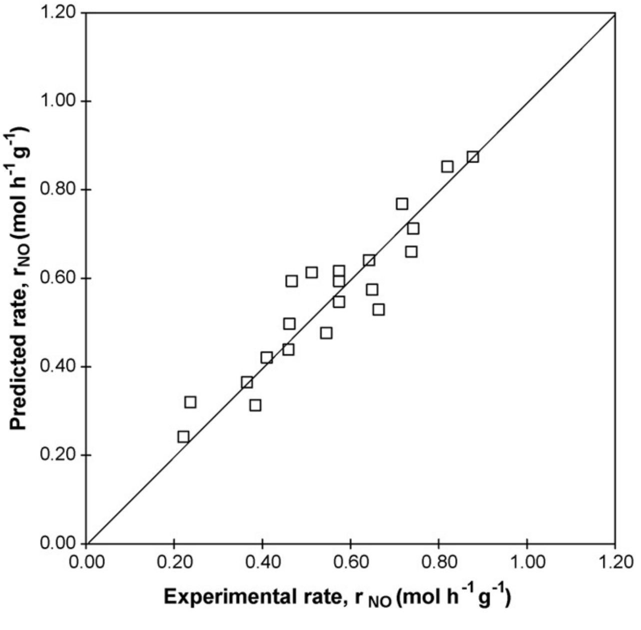

Fig. 5. Correlation between experimental and predicted rates for the $NO + H_2$ reaction on pre-reduced $Pd/LaCoO_3$ in H_2 at 450 °C according to a bi-functional mechanism.

5. Conclusion

This study reports a kinetic investigation of the $NO + H_2$ reaction on palladium supported over reducible material, such as $LaCoO_3$. An extensive reduction of $Pd/LaCoO_3$ leads to the coexistence of metallic Pd and Co particles dispersed on La_2O_3.

The interaction between the reduced material and palladium particles drastically changes the kinetic behaviour of Pd in comparison with a classical alumina support. In this latter case, the active sites are mainly composed of palladium and the reduction of NO by H_2 can be correctly modelled according to a Langmuir–Hinshelwood mechanism earlier established for noble metals. On the other hand, such a mechanism does not prevail on Pd/$LaCoO_3$ pre-activated in H_2 at 450 °C. In that case, a bi-functional mechanism would likely occur in agreement with previous findings suggesting a local reduction of La_2O_3 in contact with palladium yielding anionic vacancies at the interface Pd/La_2O_3 [20,21].

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