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Catalytic reduction of NO by CO over Pd - doped Perovskite-type catalysts

Research Article

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Abstract: The perovskite type oxides (nominal formula $LaTi_{0.5}Mg_{0.5}O_3$) with addition of Pd were prepared by annealing the ethanol solution of precursors in nitrogen flow at 1200°C and characterized by X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption of NO (NO-TPD). Their activity was evaluated for NO reduction by CO under stoichiometric and oxidizing conditions and for direct decomposition of NO. Pd substituted samples exhibited high NO reduction activity and selectivity towards N_2. Nearly complete elimination of NO was achieved at 200°C. Two simultaneous reactions, NO reduction by CO and direct decomposition of NO as well as two forms of NO adsorption were observed on the surface of Pd substituted perovskite samples. The distribution of Pd in different catalytically active sites or complexes on at the catalyst surface may be responsible for the proceeding of two reactions: NO reduction with CO and direct NO decomposition.

Keywords: *NO reduction • NO decomposition • perovskites • palladium catalist*

1. Introduction

The emission of nitrogen oxides from industrial gases or from motor vehicles is an important contemporary problem in relation to environmental protection and public health. One of the ways to reduce nitrogen oxides proposed by modern chemistry is their catalytic conversion to nitrogen. Much attention has been paid in the last decades to perovskite type mixed oxides as candidates for NO reduction due to their red-ox properties and non-stoichiometric structure. Among various perovskite types with transition metal ions in B position, the mixed oxides containing iron [1-3] and copper [4-8] are considered the most active catalysts in NO reduction with CO.

In their studies of Pd perovskite catalysts for automotive emission control, Tanaka *et al.* [9] and Nishihata *et al.* [10] found that in the systems $LaFe_{0.90}Pd_{0.10}O_3$, $LaCo_{0.90}Pd_{0.10}O_3$, $LaFe_{0.54}Co_{0.36}Pd_{0.10}O_3$ and $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$, palladium was not only dispersed at the surface of perovskite crystals but also formed a solid solution in the perovskite type oxides. Furthermore, if palladium perovskite catalysts are cycled between oxidative and reductive conditions, which are typical of automotive emissions, palladium reversibly goes into and out of the perovskite structure. Zhou *et al.* [11] have shown that excellent three-way catalytic activity of $Pd/LaFe_{0.8}Co_{0.2}O_3$ and $LaFe_{0.77}Co_{0.17}Pd_{0.06}O_3$ is obtained due to hydrocarbon steam reforming.

Structural evolution of $LaCoO_3$ and their surface modification by palladium addition, under various controlled atmospheres, particularly during the reduction of NO by hydrogen under lean conditions was reported by Twagirashema *et al.* [12]. On reduced perovskite-based catalysts a reoxidation process occurs

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at low temperature (around 100°C) in the absence of O_2 leading to the formation of N_2 and/or N_2O [13]. Generally, the reduction of NO by CO is displayed by a two-step reaction involving the intermediate formation of nitrous oxide (N_2O) according to the following sequences [14]:

$$2CO + 2NO = N_2 + 2CO_2 \tag{1}$$
$$CO + 2NO = N_2O + CO_2 \tag{2}$$
$$CO + N_2O = N_2 + CO_2 \tag{3}$$

Alternately NO decomposition can occur at high temperature.

In our recent study [15] we established that the Ag+Pd/SiO_2 catalyst showed a high activity in NO reduction with CO and direct decomposition of NO.The presence PdO in these catalysts allows the elimination of NO. The process of this elimination includes reduction of NO with CO at temperatures up to 200°C as well as direct decomposition of NO at higher temperatures. Analogous results have been obtained with active carbon-supported nickel catalysts for direct decomposition of nitrogen oxide [16]. It was of interest to see whether this effect would be found with other palladium catalysts. For that reason, the purpose of the present work was to study the catalytic reduction of NO with CO over catalysts $LaTi_{0.5}Mg_{0.5}O_3$ with Pd addition in a stoichiometric mixture, in a slightly oxidative medium and in direct decomposition of nitrogen oxides in inert atmosphere.

2. Experimental Procedures

2.1. Catalyst preparation

The perovskite samples with the nominal formula $LaTi_{0.5}Mg_{0.5}O_3$ and the samples in which the Mg is partially replaced by Pd were prepared starting from the ethanol solution of appropriate amounts of $La(NO_3)_3$•$6H_2O$ (99% Alfa Aesar), $Mg(NO_3)$•$6H_2O$ (99.97% Alfa Aesar), $TiCl_4$ (10% solution in 20-30% hydrochloric acid, Sigma-Aldrich), and $Pd(NO_3)_2$ (99.95% solution, Alfa Aesar). The obtained precursor was dried and thermally treated stepwise up to a temperature of 1200°C. The thermal treatment was performed in nitrogen with a low concentration of O_2 (between 100-150 ppm). The preparation procedure was described in detail previously [17]. In this way samples with the desired nominal formula $LaTi_{0.5}Mg_{0.5-x}Pd_xO_3$ ($0 \le x \le 0.1$) were synthesized. In order to study the samples thus obtained with respect to the direct decomposition of NO, they had to contain a higher Pd percentage. We divide the samples into such with (i) a higher (4.6 wt.% Pd) and (ii) a lower (2.34 wt.% Pd) palladium content.

2.2. Adsorption studies

The surface area of the samples was determined by the BET method at the temperature of liquid nitrogen.

2.3. X-ray diffraction

The powder diffraction data were collected at room temperature using a Philips PW 1700 diffractometer in a Bragg-Brentano geometry with a curved graphite monochromator, CuKα radiation (λ = 1.5418 Å) and step scan mode (range: 4-90° 2θ, step time 0.50 s, step width, 0.02°). The program LSUCRIPC was used for calculating the unit cell parameters.

2.4. XPS measurements

The XPS measurements were performed in a VG Escalab II spectrometer using monochromatic MgKα radiation (*hv* =1253.6 eV). The pressure in the analysis chamber was 1×10^{-10} Torr. Electrostatic surface charging was observed in all investigated samples owing to their poor electric conductivity. Therefore, C 1s, with a binding energy (BE) of 285.0 eV from carbon contaminants was used as a reference level. The binding energies reported here are accurate to ±0.2 eV. XPS surface compositions were calculated from photoelectron peak areas of each element after correcting for instrument parameters.

2.5. Catalytic activity measurements

Catalytic activity experiments in NO reduction with CO were carried out in the flow apparatus described in [18] in the temperature range 25-400°C. Temperature-programmed desorption (TPD) experiments were carried out on the same catalytic apparatus at a heating rate of 13°C min^{-1} in an Ar flow. Argon (purity 99.99 vol.%) was used as a carrier gas at a total gas-flow rate of 433 cm^3 min^{-1} (GHSV = 26 000 h^{-1}). A catalyst amount of l cm^3 (particle size 0.3-0.6 mm) was used in all experiments and placed into the reactor with a quartz tube (d=10 mm). The catalytic activity tests were performed using three gas mixtures: (i) NO+CO+Ar, with a red-ox index (RO) = $[CO]_{inlet}$ / $[NO]_{inlet}$=1 (1200 ppm NO and 1200 ppm CO) *i.e.* conditions close to the stoichiometry; (ii) NO+CO+Ar, with a red-ox index (RO) = 0.6 (800 ppm CO and 1300 ppm NO) *i.e.* conditions close to oxidizing; (iii) NO+Ar, containing 1200 ppm NO. Before a catalytic test, the catalysts were treated in an Ar flow at 400°C for 1 h and cooled to room temperature. After stabilization at room temperature in a NO+CO+Ar mixture and isothermal desorption in Ar flow with a rate of 433 cm^3 min^{-1}, temperature programmed desorption (TPD) was carried out in the temperature range 25- 400°C and the TPD spectra of NO, CO and CO_2 were registered. After that the reactor was cooled to 50°C. The sequence

Table 1. Pd content, specific surface area and phase composition of the synthesized samples.

Sample	Pd content, (mass. %)	S_{BET}, (m^2 g^{-1})	Phase composition, XRD
$LaTi_{0.5}Mg_{0.5}O_3$		5.1	Perovskite
$LaTiMgO_3$ (2.34 wt.% Pd)	2.34	4.9	Perovskite; traces of Pd^0; La_4PdO_7
$LaTiMgO_3$ (4.6 wt% Pd)	4.60	5.0	Perovskite; traces of Pd^0

Table 2. The atomic ratios of elements in the surface layers obtained by XPS.

Sample	O/La	Ti/La	Mg/La	Pd/La
$LaTi_{0.5}$ Mg $_{0.5}O_3$	3.53	0.25	0.49	-
$LaTiMgO_3$ (2.34 wt.% Pd)	4.72	0.41	0.76	0.04
$LaTiMgO_3$ (4.6 wt% Pd)	4.17	0.29	0.75	0.10

of this set of experiments involved a reaction stage (NO+CO+Ar) and an isothermal desorption stage (Ar flow with a rate of 433 cm^3 min^{-1}) carried out at the desired temperatures in the range from 50 to 400°C. For comparison, $LaTi_{0.5}Mg_{0.5}O_3$ without Pd was investigated under the same conditions.

The concentrations of NO, CO and CO_2 were continuously measured by gas analysers and the data were collected by a CSY-10 microprocessor computer system. The inlet concentration of CO was controlled by an “Infralyt 2106” NDIR gas analyser. The outlet concentrations of NO and CO were controlled by UNOR 5 (Maihak) and that of CO_2, by Infralyt 2106. A Specord 75 IR spectrophotometer with a 1 m folded path gas cell (Specac) was used for determination of the N_2O content outlet. The N_2 concentration in the outlet gas was determined on the basis of the material balance with respect to NO consumption. In a case of direct decomposition of NO, the N_2 and O_2 contents were controlled periodically by a Pye Unicam 104 (U.K.) gas chromatograph by column with a molecular sieve. The transient response method [19] was used to study the interaction of the gas phase with the catalyst surface.

3. Results and Discussion

Table 1 shows the phase composition, the Pd content and the specific surface area of the synthesized perovskite samples.

According to the XRD analysis all samples are almost single phase perovskites with orthorhombic structure [17]. During the thermal treatment of the catalyst precursor to the temperature of 1200^{0}C, besides incorporation of Pd^{2+} in the perovskite structure, interaction of palladium with precursor components is also possible. In both Pd samples (Table 1) besides in perovskite structure, a part of palladium is present as Pd^0 and as La_4PdO_7 in the sample with a lower content of palladium only, high purely perovskite phases are not obtained, this meaning that their actual stoichiometry does not quite agree with the desired chemical composition, the samples are denoted according to the weight content of palladium, namely $LaTiMgO_3$ (2.34 wt.%Pd) and $LaTiMgO_3$ (4.6 wt.% Pd).

The relatively small specific surface area (about 5 m^2 g^{-1}) is not unexpected in view of the high synthesis temperature of the samples.

Fig. 1 illustrates the results of XPS analysis of $LaTi_{0.5}Mg_{0.5}O_3$, $LaTiMgO_3$ (2.34 wt% Pd) and $LaTiMgO_3$ (4.6 wt.% Pd). The position of Pd 3d peaks at 336.1 eV and 336.4 eV is in very good agreement with the BE reported for PdO (Pd^{2+}) [20]. The BE of 834.9 eV for La $3d_{5/2}$ corresponds to that of La_2O_3 (La^{3+}) reported in the literature [21]. The position of Ti $2p_{3/2}$ is also in very good agreement with the binding energy reported for Ti^{4+} in TiO_2, $BaTiO_3$ and $CaTiO_3$ [20]. The BE of the Mg 2p peak is lower than 49.6 eV, referenced for Mg^0. It is most likely that this notable deviation in BE originates from electron transfer to the valence orbital of Mg in the perovskite structure, which leads to a decrease in BE to values lower than that for Mg^0 [22]. The O1s spectrum in all samples consists of a doublet, which implies that at least two kinds of oxygen species are present at the surface. The first of these peaks (at lower BE (529.5 - 529.7eV)) is characteristic of lattice oxygen (O^{2-} species). The second peak (at 531.5 eV) could be assigned to adsorbed oxygen, OH^- and CO_3^{2-} groups.

XPS revealed the presence of Pd^{2+} in surface layers. The cooling of the samples in nitrogen flow with an extremely low concentration of O_2 (between 100 and 150 ppm) leads to complete reoxidation of palladium in the surface layers but according XRD analysis suppresses the complete reoxidation of Pd^0 in the bulk. PdO phase was not detected by XRD probably because of the extremely small particle size and thin layers of PdO formed at the surface of perovskite crystals.

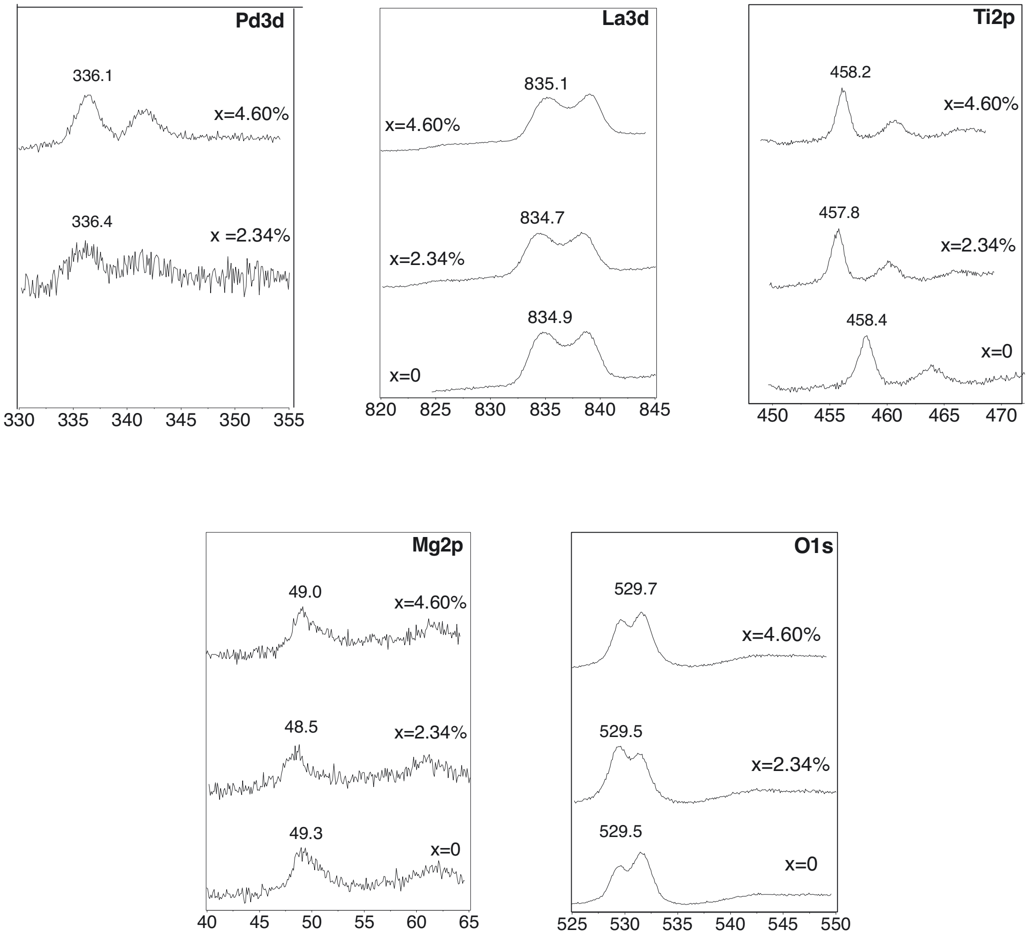
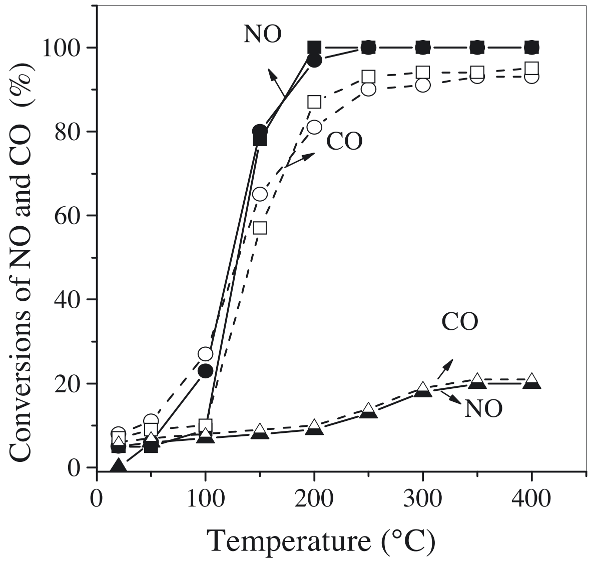


Figure 1. The X-ray photoelectronic spectra of $LaTi_{0.5}Mg_{0.5}O_3$ without Pd, $LaTiMgO_3$ with 2.34 wt.% Pd and $LaTiMgO_3$ with 4.6wt.% Pd samples.



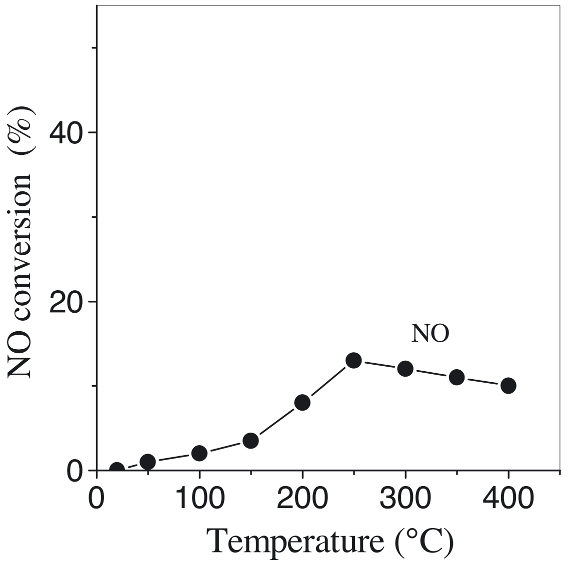


Figure 2. NO conversion and CO oxidation as a function of temperature for the samples: (NO-▲; CO-Δ) $LaTi_{0.5}Mg_{0.5}O_3$ without Pd, (NO-●; CO-○)$LaTiMgO_3$ with 2.34 wt.% Pd and (NO-■; CO-□) $LaTiMgO_3$ with 4.6 wt.% Pd in NO+CO+Ar mixture with RO=1.

Figure 3. NO conversion as a function of temperature for the catalyst $LaTiMgO_3$ with 2.34 wt.% Pd in a NO+Ar mixture.

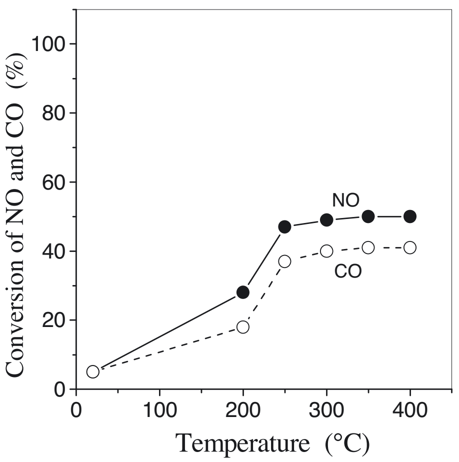


Figure 4. NO conversion and CO oxidation as a function of temperature for the catalyst $LaTiMgO_3$ with 2.34 wt.% Pd in a NO+CO+Ar mixture with RO=0.6.

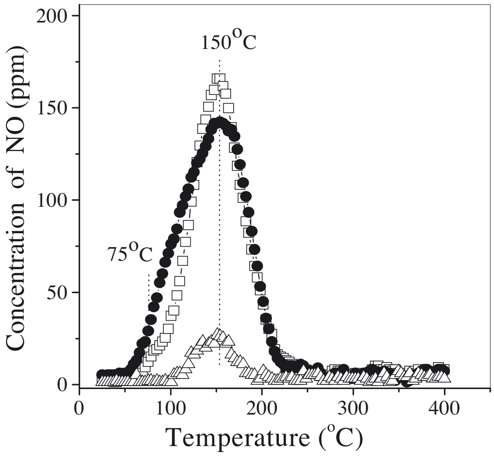


Figure 5. TPD spectra of NO for (Δ) $LaTi_{0.5}Mg_{0.5}O_3$ without Pd, (●) $LaTiMgO_3$ with 2.34 wt.% Pd and (□) $LaTiMgO_3$ with 4.6 wt.% Pd.

Fig. 2 illustrates the dependence of the conversion degree of NO and oxidation of CO on temperature for all synthesized samples.

As can be seen in Fig. 2, replacement of Mg by Pd in $LaTi_{0.5}Mg_{0.5}O_3$ enhances the NO reduction from about 10% to nearly complete elimination of NO at 200°C. The Pd content in the samples has a small influence on the NO reduction. The NO reduction and CO oxidation degrees are almost the same for the perovskite matrix $LaTi_{0.5}Mg_{0.5}O_3$. However, over palladium perovskite the conversion of NO above 150°C is higher than that of CO. Pisanu *et al.* [23] reported that NO conversion was always higher than that of CO, which is typical of the NO+CO reaction over supported Pd catalysts and is in accordance with the formation of N_2O as a reaction product. It is important to point out that in the reaction products obtained in the presence of all the investigated perovskite catalysts, no N_2O was detected. The results present evidence that the samples under consideration begin to show activity above 150°C. It is interesting that at these and higher temperatures no formation of N_2O has been established. It is known [18] that during reduction of NO with CO, *e.g.* in studies of spinel catalysts, N_2O formation passes through a maximum, however at lower temperatures (about 130°C).

The NO reduction in the absence of a reducing agent (NO+Ar mixture) and in an deficit of reducing agent (R=0.6) *i.e.* under oxidizing conditions for $LaTiMgO_3$ (2.34 wt.% Pd) is presented in the Fig. 3 and Fig. 4, respectively. As can be seen in Fig. 3, direct decomposition of NO, although to a low extent, takes place at temperatures higher than 150°C. The decomposition of NO in the gas mixture containing excess NO is evidenced over the whole temperature range investigated (Fig. 4). Similar results are obtained for the sample with a higher content of Pd (4.6 wt.%). Gas-chromatographic analysis showed the presence of N_2 and O_2 when studying the samples for direct NO decomposition. Prolonged experiments (of about 3 h) revealed no activity drop, *i.e.* no Pd oxidation took place.

Fig. 5 shows TPD spectra obtained after a NO+CO reaction at 25°C for $LaTi_{0.5}Mg_{0.5}O_3$, $LaTiMgO_3$ (2.34 wt.% Pd) and $LaTiMgO_3$ (4.6 wt.% Pd) samples. A NO desorption peak centered at 150°C is found in the TPD profiles of all samples investigated. The intensity of this peak is significantly higher for Pd perovskite than for $LaTi_{0.5}Mg_{0.5}O_3$ and increases with the Pd content. TPD patterns of Pd substituted samples show an additional peak at a lower temperature, centered at about 75°C.

The transient response curves of the reactants NO and CO and the products CO_2 and N_2 obtained for all samples upon stepwise temperature increase from 100 to 200°C are presented in Figs. 6a, 6b and 6c, respectively. The transient experiments are performed in the stoichiometric gas mixture NO + CO + Ar (RO=1).

As can be seen in Fig. 6a, the response curves of the reactants NO and CO and the products CO_2 and N_2 of the sample $LaTi_{0.5}Mg_{0.5}O_3$ are of instantaneous type response at all the investigated temperatures. According to Kobayashi's classification [19] this means that the surface reaction or adsorption of reactants is the rate determining stage. The absence of desorption curves at the stop stage indicates that the surface reaction is the rate-controlling step in the reaction mechanism. The response curves for NO, CO, CO_2 and N_2 obtained in a stoichiometric gas mixture of NO+CO+Ar (RO=1) for Pd substituted samples with 2.34 wt.% and 4.6 wt.% Pd are

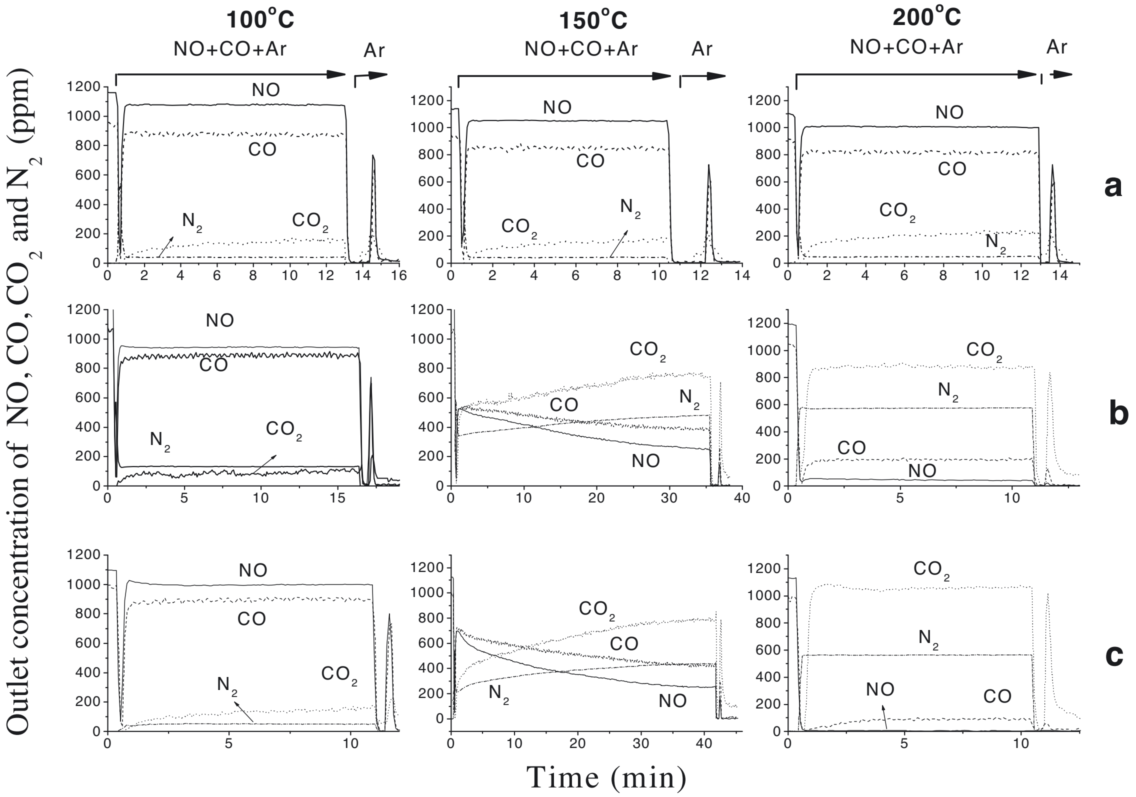


Figure 6. Response curves of NO, CO, CO_2 and N_2 for: (a) $LaTi_{0.5}Mg_{0.5}O_3$ without Pd, (b) $LaTiMgO_3$ with 2.34 wt.% Pd and (c) $LaTiMgO_3$ with 4.6 wt.% Pd) samples.

presented in Figs. 6b and 6c, respectively. It is obvious that the response curves for both kinds of Pd substituted samples differ from those obtained for the sample without Pd. Below 150°C both samples show an instantaneous type response of the reactants, which indicates that the surface reaction can be the rate determining step. At a higher temperature there is also an overshot response for NO, which is especially pronounced for both samples at 150°C.

3.1 Discussion

From the result it appears that besides the NO reduction with CO as the main reaction,

$$2NO + 2CO = N_2 + 2CO_2 \tag{4}$$

direct NO decomposition

$$2NO = N_2 + O_2 \tag{5}$$

simultaneously proceeds at the surface of Pd perovskite samples. This fact implies the presence of different active sites at the surface of Pd containing perovskite which are responsible for the proceeding of these reactions. Similar results are obtained in the study of NO reduction by CO over an $Ag+Pd/SiO_2$ catalyst [15].

The presence of two forms of NO adsorption on Pd doped samples indicates that different catalytically active sites are probably formed at the surface, which are responsible for the reduction of NO and the decomposition of NO. It is important to point out that desorption peaks for CO and CO_2 are not detected.

The change in rate-controlling step is associated with a change in the reaction mechanism. Furthermore, from Figs. 6b and 6c it can be seen that the CO_2 response curves approach the monotonic type response above 150°C. This indicates that the rate determining step is a combination of surface reaction and product desorption. From the previous results, it can be seen that for $LaTi_{0.5}Mg_{0.5}O_3$ the response curves for the reactants and the products are instantaneous. However, for Pd perovskite samples the response curve types at 150°C become different from those for the reactants.

Therefore, depending on the character of the response curves obtained in the study of Pd- perovskite type samples up to 150°C the surface reaction is the rate-determining stage and above 150°C this is a combination of surface reaction, product desorption and regeneration of active surface species. This complicated picture can be ascribed to the fact that on the surface of the catalysts under the investigation both reactions take place: NO reduction with CO and direct decomposition of NO, the rate controlling step in both reactions being mainly the surface reaction.

4. Conclusions

Pd perovskites have exhibited a high NO reduction activity and selectivity towards N_2. Nearly complete elimination of NO is achieved at 200°C. Two simultaneous reactions, NO reduction by CO and direct decomposition of NO as well as two forms of NO adsorption are observed at the surface of Pd substituted perovskite samples.

The Pd content has a small influence on the NO reduction. The NO reduction activity of the sample with 2.34 wt.% Pd, despite the lower palladium content and lower exposure to Pd atoms in the surface layers is close to that of the sample with 4.6 wt.% Pd. The enhanced activity of the sample with a lower degree of Pd substitution can be ascribed to the higher dispersion of Pd^{2+} incorporated in the perovskite structure and in PdO and Pd^0 phases. The high dispersion of Pd^0 and PdO phases due to intimate contact with perovskite crystals implies the higher contribution of the lattice oxygen and consequently easier local changes in the oxidation state of palladium. Due to the distribution of Pd in different catalytically active sites or complexes, Pd may be present at the catalyst surface which can be responsible for the simultaneous proceeding of the two reactions: NO reduction with CO and direct NO decomposition.

Acknowledgements

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