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The effect of temperature on NO_x reduction by H_2 in the presence of excess oxygen on a Pt/Al_2O_3 monolithic catalyst

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ABSTRACT

This study examined the reduction of NO_x by H_2 over a Pt/Al_2O_3 catalyst coated onto a monolith as a function of temperature. The formation of N_2O began at a low temperature due to the chemisorption of NO on Pt metal and its resulting oxidation at the Pt active sites. The formation of N_2 was possible at higher temperatures because at the high temperatures, the reaction rate for N_2 formation was higher than the reaction rate for N_2O formation. The formation of NO_2 was predominant above 150 °C due to the excessive oxidation activity of the catalyst. The formation of N_2O at low temperatures and that of N_2 at high temperatures were found to be strongly related to the Pt loading and the temperature range in which the reductive activity was obtained, respectively. Therefore, both reductive conditions and an adequate reaction temperature are important factors for the selective formation of N_2 from the reduction of NO on a Pt catalyst. The temperature-dependent change in the oxidation state of Pt during the reduction of NO was also examined to determine the mechanism for the reduction of NO_x by H_2. In addition, the reaction conditions for the selective reduction of NO_x to N_2 were determined.

1. Introduction

Lean-burn combustion was developed to reduce fuel consumption and CO_2 emissions. However, under the combustion conditions, NO_x cannot be purified sufficiently using the conventional three-way catalysts. Over the last three decades, the selective catalytic reduction (SCR) of NO_x and its underlying mechanisms have been examined extensively [1]. Ammonia and hydrocarbons are considered to be the best reducing agents in this process but hydrogen has also been reported to be a very effective reducing agent [2]. Hydrogen is one of the exhaust gases emitted by automobiles and can easily be generated by an on-board compact reformer used in a fuel cell system [3,4]. In particular, supported platinum catalysts were reported to be most active for the lean de-NO_x reaction at low temperatures where the reduction of NO by H_2 under oxygen-rich conditions was examined [5]. Costa et al. reported NO reduction with H_2 on Pt/Al_2O_3 and the effect of the Pt loading over a $Pt/MgO–CeO_2$ catalyst at different reaction temperatures [6,7]. Furthermore, they reported significant mechanistic isotopic studies of the H_2-SCR of NO over Pt-supported mixed-oxide and perovskite-type materials (e.g., $Pt/MgO–CeO_2$, Pt/La–Sr–Ce–Fe–O, Pt/La–Ce–Mn–O) using Steady State Isotopic Transient Kinetic Analysis (SSITKA) [8,9]. Recently, Efstathiou et al. have reported the significance of H_2-SCR compared to NH_3-SCR and HC-SCR considering the progressive demand for hydrogen with a growth rate of approximately 10% a year in many industrial installations [10]. In addition, the selective catalytic reduction of NO_x by CH_4 in real exhaust gas of a lean-burn gas engine was investigated [11].

Therefore, this study investigated the temperature-programmed reduction of NO_x by H_2 over a Pt/Al_2O_3 catalyst with various Pt loadings and in the presence of excess oxygen. In particular, the NO_x reduction experiments were carried using a Pt/Al_2O_3 catalyst coated onto a monolith. This is because the monolithic catalyst offers a lower pressure drop compared with the traditional catalysts used for gas-phase reactions, which obviously is quite advantageous in vehicle engine emission control.

2. Experimental

2.1. Catalyst preparation

Modern emission control catalysts utilize monolithic flow-through supports coated with a high surface area of inorganic oxides and precious metals. In this study, ceramic honeycomb (400 cells/in.^{2}, 2 cm × 2 cm × 3 cm, Ceracomb Co., Korea) was used as the monolithic support on which aluminum oxide (Al_2O_3, Aldrich Co.) had been washcoated. The washcoat was prepared with 4 g of aluminum oxide and 20 ml of alumina sol (Al_2O_3 10 wt%, AS-

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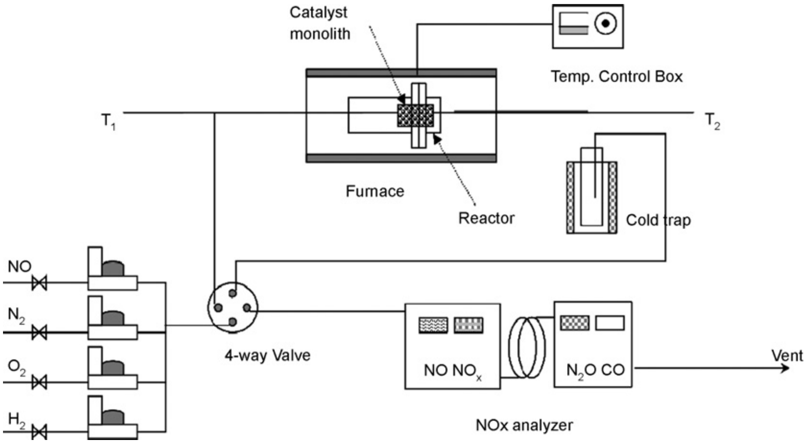

Fig. 1. Schematic diagram of the experimental apparatus.

200, Nissan Chemical Co., Japan). The washcoat was applied to the monolith from water-based slurry, dried at 120 °C and calcined at 550 °C. Finally, Pt was impregnated on the alumina using an incipient wetness method from an aqueous solution of $H_2PtCl_6{\cdot}xH_2O$, and its loading was controlled by adjusting the concentration of the $H_2PtCl_6{\cdot}xH_2O$ aqueous solution. The catalyst was calcined at 550 °C and reduced in an N_2 stream containing H_2 (10%) at 350 °C before confirming its catalytic activity.

2.2. *Catalyst characterization*

The elemental platinum concentration was measured by ICP-AES (ICPS/7500, Shimadzu). The discrepancy between the intended and ICP-measured loading suggests that some of the solution had been lost during the impregnation process. The XPS spectra were recorded on a VG-ESCA2000 spectrometer with Mg Kα X-rays as the photon source (2253.6 eV). The power of the X-ray source was set to 300 W. The binding energies (BEs) were referenced to the C (1s) peak at 284.8 eV.

2.3. *Experimental apparatus and methods*

The activity test was carried out in a fixed-bed flow reactor system. Fig. 1 shows a schematic diagram of the reaction apparatus. Typically, the reactants gas consisted of 2000 ppm NO, 1% H_2, 5% O_2 with the balance made up of N_2 to simulate the exhaust gas from vehicles powered by lean-burn engines. The total flow rate was 2400 cm^3 (STP)/min, resulting in a GHSV of 12,000 h^{-1}. The reaction temperature was increased from 20 to 350 °C with a ramp of 5 °C/min.

On-line NO_x analyzers (ULTRAMAT 23 for NO and NO_x analysis, ULTRAMAT 6 for N_2O and CO analysis, SIEMENS Co., Germany) were used to examine the composition of the product. And, the produced N_2 concentration was calculated on the base of N-balance. The N-balance, NO_2 concentration, N_2 concentration and N_2 selectivity are defined as follows:

$$\text{N-balance}\,(\%) = \frac{\{(\text{NO conc.})_{\text{out}} + (\text{NO}_2\ \text{conc.})_{\text{out}} + 2(\text{N}_2\text{O conc.})_{\text{out}}\}}{(\text{NO conc.})_{\text{in}}} \times 100 \tag{1}$$

$$\text{NO}_2\ \text{conc.}\,(\text{ppm}) = (\text{NO}_x\ \text{conc.}) - (\text{NO conc.}) \tag{2}$$

$$\text{N}_2\ \text{conc.}\,(\text{ppm}) = \frac{\{2000 - (\text{NO conc.}) - (\text{NO}_2\ \text{conc.}) - 2(\text{N}_2\text{O conc.})\}}{2} \tag{3}$$

$$\text{N}_2\ \text{sel.}\,(\%) = \frac{(\text{N}_2\ \text{conc.})}{\{(\text{N}_2\ \text{conc.}) + (\text{N}_2\text{O conc.})\}} \times 100 \tag{4}$$

In the above equations, we neglected an extra term in the N-balance which came from the surface adsorbed species on the catalyst because we already confirmed that the N-balance was almost equaled to 100% at the temperatures lower than 50 °C.

3. Results and discussion

3.1. *Effect of temperature*

The reduction of NO by H_2 in the presence of oxygen was examined over a 0.3 wt% Pt/Al_2O_3 catalyst with increasing temperature. Fig. 2 shows the temperature-programmed NO reduction by H_2 over the catalyst. There were three characteristic temperature regions with distinct catalytic activities. Only N_2O was formed in the lowest temperature region of 20–35 °C (1st region) without external heating. The formation of N_2O in this temperature range originated from the chemisorbed NO molecules on Pt metal leaving surface-oxidized Pt particles [12]. Therefore, the concentration of N_2O produced in this temperature region followed a volcano-type curve depending on the proportion of Pt oxidized by NO chemisorption. However, a small amount of N_2O was still formed in this temperature range because hydrogen continued to reduce the oxidized surface of the Pt particles, thus allowing the further adsorption of

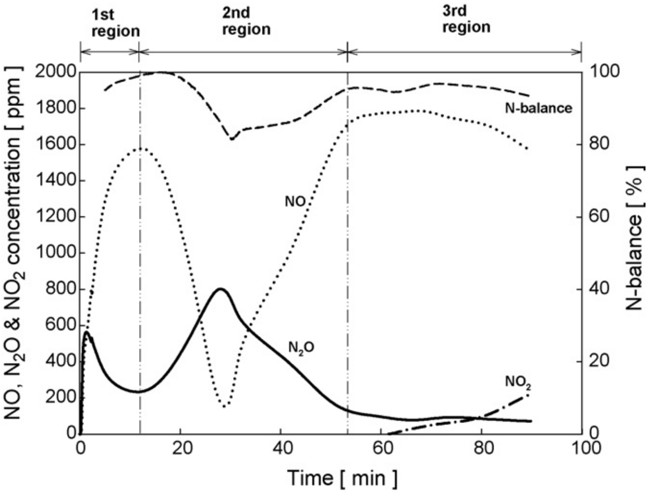

Fig. 2. Temperature-programmed NO reduction by H_2 over 0.3 wt% Pt/Al_2O_3.

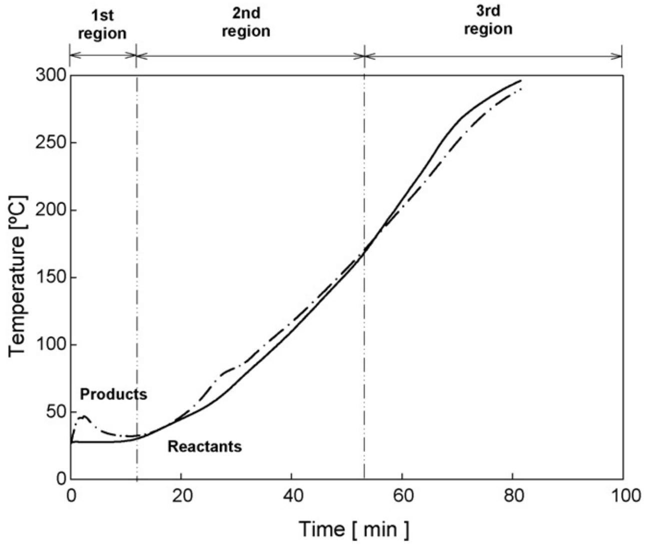

Fig. 3. Temperature changes of reactants and products during the reduction of NO.

NO. Molecular oxygen in the gas phase did not appear to be involved in this reaction [8,9]. Fig. 3 also shows the temperature variations of the reactants and products. The temperature of the products was higher than that of the reactants when N_2O was formed, which was attributed to the chemisorption of NO to the Pt surface. As the heats of formation of NO and N_2O at 25 °C were 90.4 and 81.6 kJ/mol, respectively, the catalytic reaction of NO towards the formation of N_2O was exothermic. Roberts suggested the following mechanism for the formation of N_2O [13]:

$$N(a) + NO(a) \rightarrow N_2O(a) \tag{5}$$

$$NO(g) \rightarrow (NO)_2(a) \rightarrow N_2O(a) + O(a) \tag{6}$$

For a Pt (1 1 1) surface, the activation energy barrier for the reaction between the chemisorbed nitrogen atoms, N(a), and the adsorbed nitric oxide, NO(a) (Eq. (5)) was reported to be 1.8 eV (=2.9×10^{-22} kJ), which is considered to be too high to account for the formation of N_2O at temperatures <100 °C [13]. However, for the formation of N_2O through the dimer $(NO)_2(a)$ (Eq. (6)), the barrier was much lower, 0.46 eV (=0.74×10^{-22} kJ), and is believed to be the favored mechanism for the formation of N_2O at low temperatures [13]. This explanation fits well with the above results for the formation of N_2O at low temperature.

In the intermediate temperature region of 35–150 °C (2nd region), there was a second phase of N_2O formation that strongly depended on the reaction temperature. At this higher temperature, hydrogen reduced the Pt active sites oxidized by the NO chemisorption. These reduced Pt active sites produced more N_2O. Costa et al. suggested that in the case of $Pt/La_{0.5}Ce_{0.5}MnO_3$ and $Pt/MgO–CeO_2$ catalysts, the reduction of the two active NO_x species located within the metal–support interface zone occurred through hydrogen spillover from the Pt to the support surface [8,9]. N_2 and N_2O were produced in this temperature range and the formation of N_2 was confirmed by the N-balance being <100%, as shown in Fig. 2. The formation of N_2 began at 42 °C and became predominant compared with the formation of N_2O at temperatures >80 °C because the energy state of the reactants was high enough for the formation of N_2 in this temperature range. It was reported that the selectivity to N_2 increased at temperatures >50 °C in a feed composition containing 1000 ppm NO, 1% H_2 and 2% O_2, while the selectivity to N_2O decreased and no NH_3 was formed at an O_2 concentration >3% for Pt/Al_2O_3 and Pt/SiO_2 catalysts [14]. In particular, the order, E_{a,N_2} (activation energy of N_2 formation, 77 kJ/mol) > E_{a,N_2O} (activation energy of N_2O formation, 45 kJ/mol), given by Frank et al. corresponds well with the present results [5]. According to Burch et al. considerably more N_2O was produced at low temperatures than N_2 but the formation of N_2 was favored at higher temperatures because, the dissociation of NO on Pt was facilitated at higher temperatures, thus favoring the formation of N_2 [14].

Table 1
Effect of the Pt loading on the formation of N_2O at low temperatures

Pt loading amount (wt%)	Reductive activity in 1st region maximum N_2O concentration (ppm)
0.02 (0.028)[a]	0
0.1 (0.12)	275
0.2 (0.19)	563
0.3 (0.33)	625
0.5 (0.49)	875

[a] The number in parenthesis was the value which was obtained by ICP.

Above 150 °C (3rd region), the formation of NO_2 was predominant due to the excessive oxidation activity of the catalyst. At this stage, no reductant was available, because the molecular oxygen oxidized all the hydrogen in the gas phase hence, the NO oxidation to NO_2 was predominant [15]. It was reported that 83% of the NO was oxidized to NO_2 with 10% O_2 over Pt/Al_2O_3 at 200 °C [16]. Macleod also reported that the level of NO_x reduction decreased and NO_2 formation was observed above the temperatures required for hydrogen light-off and maximum NO_x conversion [17].

3.2. *Effect of Pt loading*

The Pt loading was varied from 0.02 to 0.5 wt% to determine its effect on the reductive activity of the catalyst. It was found that the first phase of reductive activity, the formation of N_2O in the low temperature range of 20–35 °C, was strongly related to the Pt loading. The Pt dispersion would not vary much with increasing Pt loading because of the narrow, low-loading range examined, which resulted in an increase in the number of surface Pt/g. As the Pt loading was increased, the number of sites available for NO chemisorption increased. Therefore, the concentration of N_2O produced increased linearly. Table 1 shows the effect of the Pt loading on the reductive activity of the catalysts at low temperatures.

Table 2 shows the second phase of the reductive activity for the formation of N_2O and N_2 at high temperature. As shown in Table 2, the reductive activity was related not to the Pt loading but to the reaction temperature. Less N_2O and more N_2 were formed in the reductive activity shown in the higher temperature range. However, more N_2O and less N_2 were formed in the lower temperature range. It is clear that the formation of N_2 was more favorable at high temperatures than N_2O. This observation also concurs with the results reported by Burch et al., in which the $N_2/(N_2+N_2O)$ ratio increased almost linearly to 80% with increasing temperature from 50 to 200 °C [14]. Therefore, it is essential to develop a catalyst that

Table 2
The reductive activity in 2nd region depending on the reaction temperature

Pt loading amount (wt%)	Reductive activity in 2nd region		Temperature[a] (°C)
	Maximum N_2O concentration (ppm)	N_2 concentration (ppm)	
0.02 (0.028)	842	158 (15.8%)[b]	66
0.1 (0.12)	1028	0 (0%)	50
0.2 (0.19)	802	172 (17.7%)	78
0.3 (0.33)	929	6 (0.64%)	51
0.5 (0.49)	870	127 (12.7%)	53

[a] The temperature meant the value for obtaining the maximum N_2O formation and it was corresponding to the outlet temperature of the reactor.

[b] The number in parenthesis was N_2 selectivity.

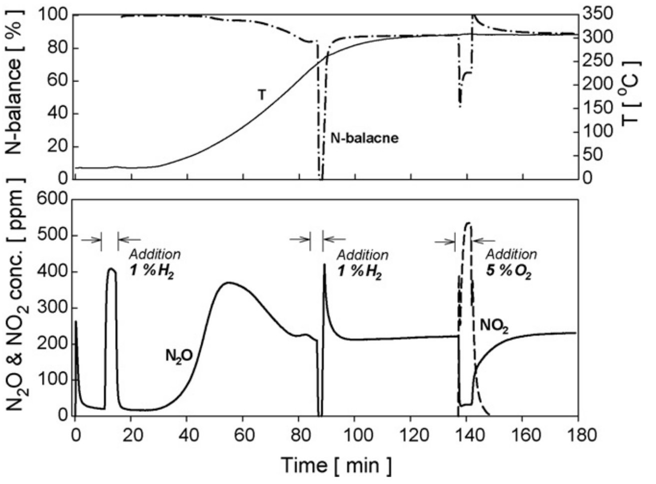

Fig. 4. Catalytic activity for the reduction of NO by the 0.3 wt% Pt/Al_2O_3 catalyst depending on the reductive and oxidative conditions.

shows reductive activity at the temperatures from 100 to 200 °C, which can be achieved by controlling the Pt loading.

3.3. Effect of reaction condition

The NO reduction activity of the catalyst under reduction/oxidation conditions was investigated. Fig. 4 shows the reductive activity of the 0.3 wt% Pt/Al_2O_3 catalyst at different reaction conditions. Initially, a 2000 ppm NO/N_2 mixture was fed into the catalyst at 25 °C and only N_2O was formed until the Pt sites had been fully oxidized to PtO through the chemisorption of NO. When 1% H_2 was introduced into the oxidized catalyst at the same temperature, N_2O was again produced in large quantities due to the reductive activity of the catalyst. However, as soon as the H_2 feed was stopped, the N_2O concentration decreased almost to zero because of the re-oxidation of Pt, and the level of NO conversion was approximately zero. The addition of 5% O_2 at this temperature did not make any difference to the activity. When the reaction temperature was increased to 350 °C without the addition of H_2 and O_2, N_2O was again formed and the maximum N_2O concentration was observed at 91 °C. This was attributed to the reduction of the oxidized Pt active sites at high temperatures, as described above.

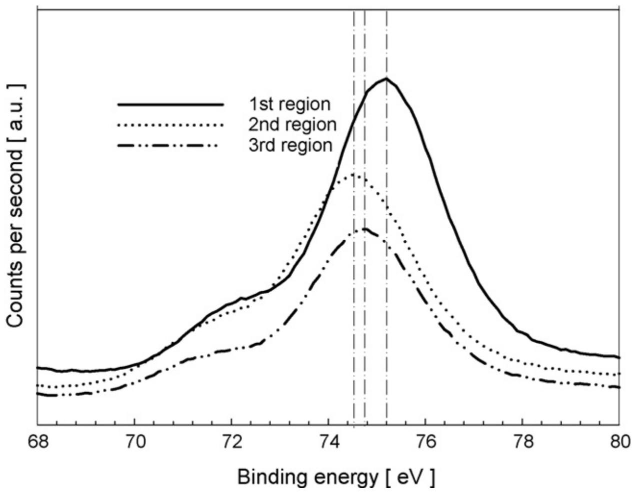

Fig. 5. XPS spectra at the 4f level of 0.3 wt% Pt/Al_2O_3 depending on the reaction temperature (1st, 2nd and 3rd regions).

Table 3
The Pt 4f$_{7/2}$ and Pt 4f$_{5/2}$ binding energies of Pt, PtO and PtO_2 [18]

	Pt 4f$_{7/2}$ (eV)	Pt 4f$_{5/2}$ (eV)
Pt	71.2	74.6
PtO	72.3	75.6
PtO_2	73.6	76.8

Furthermore, the formation of N_2 began at 66 °C and was further accelerated once the N_2O concentration began to decrease at 91 °C, which also supports the conclusion that the formation of N_2 is more favorable at high temperature than that of N_2O. At 200–315 °C, N_2O and N_2 were formed together with almost constant concentrations because there was no oxygen. When H_2 was added to the reactants in this temperature range, the N_2O concentration decreased to nearly zero and the total N-balance was also close to zero. Therefore, almost all the NO was reduced to N_2 by hydrogen at high temperatures. NO_2 was also formed when O_2 was added at high temperatures.

3.4. Pt oxidation state

In order to confirm the validity of the proposed mechanism, the Pt oxidation state of the Pt/Al_2O_3 catalyst in the different temperature regions (1st, 2nd and 3rd regions) was examined by XPS. Fig. 5 shows the XPS spectra of the 4f level of 0.3 wt% Pt/Al_2O_3 depending on the reaction temperature (1st, 2nd and 3rd regions). The Pt 4f$_{7/2}$ and Pt 4f$_{5/2}$ binding energies of Pt, PtO and PtO_2 are reported in Table 3 [18]. As shown in Fig. 5, the Pt species in the 1st region was more highly oxidized compared with the Pt species in the 2nd and 3rd regions, which is compatible with the proposed mechanism, wherein the Pt species in the 1st region was oxidized due to the chemisorption of NO resulting in the formation of N_2O. However, the Pt species in the 2nd region were reduced, which was attributed to the reduction of the oxidized Pt by H_2 at high temperatures. Hence, both N_2O and N_2 could be formed on the Pt reduced sites in the high temperature range. In the 3rd region, the Pt state was similar to that in the 2nd region. However, in this stage, the most of the Pt was used as the active sites for the oxidation of NO to NO_2, because there was no reductant available.

4. Conclusions

The following conclusions can be derived from the results of the present work:

1. The reduction of NO by H_2 was examined over a 0.3 wt% Pt/Al_2O_3 catalyst coated onto a monolith as a function of temperature because the monolithic catalyst was quite advantageous in vehicle engine emission control.
2. At low temperatures, only N_2O was formed and moreover, its formation in this temperature range originated from the NO molecules chemisorbed on the Pt metal. The formation of N_2 was predominant at temperatures over 80 °C compared with that of N_2O because at the temperatures, the reaction rate for N_2 formation was higher than the reaction rate for N_2O formation.
3. The 1st phase of the reductive activity leading to the formation of N_2O was strongly related to the Pt loading, but the 2nd phase of reductive activity leading to the formation of N_2 depended on the reaction temperature at which the reductive activity was obtained, and this temperature could be varied by controlling the Pt loading.
4. XPS confirmed that the formation of N_2O in the low temperature region was due to the oxidation of Pt caused by the chemisorp-

tion of NO and the formation of N_2 in the high temperature region was due to the reduction of the oxidized Pt by H_2.

5. Both the reductive conditions and an adequate reaction temperature are important factors for the selective formation of N_2 from the reduction of NO on the Pt catalyst.

References

[1] V.I. Parvulescu, P. Grange, B. Delmon, Catalytic removal of NO, Catal. Today 46 (1998) 233–316.

[2] T. Nanba, C. Hohno, S. Masukawa, J. Uchisawa, N. Nakayama, A. Obuchi, Improvements in the N_2 selectivity of Pt catalysts in the $NO–H_2–O_2$ reaction at low temperatures, Appl. Catal. B 46 (2003) 353–364.

[3] A. Lindermeir, S. Kah, S. Kavurucu, M. Muhlner, On-board diesel fuel processing for an SOFC-APU-technical challenges for catalysis and reactor design, Appl. Catal. B 70 (2007) 488–497.

[4] C. Severin, S. Pischinger, J. Ogrzewalla, Compact gasoline fuel processor for passenger vehicle APU, J. Power Sources 145 (2005) 675–682.

[5] B. Frank, G. Emig, A. Renken, Kinetics and mechanism of the reduction of nitric oxides by H_2 under lean-burn conditions on a $Pt–Mo–Co/\alpha\text{-}Al_2O_3$ catalyst, Appl. Catal. B 19 (1998) 45–57.

[6] C.N. Costa, V.N. Stathopoulos, V.C. Belessi, A.M. Efstathiou, An investigation of the $NO/H_2/O_2$ (lean-deNO_x) reaction on a highly active and selective $Pt/La_{0.5}Ce_{0.5}MnO_3$ catalyst, J. Catal. 197 (2001) 350–364.

[7] C.N. Costa, A.M. Efstathiou, Low-temperature H_2-SCR of NO on a novel $Pt/MgO–CeO_2$ catalyst, Appl. Catal. B 72 (2007) 240–252.

[8] C.N. Costa, A.M. Efstathiou, Transient isotopic kinetic study of the $NO/H_2/O_2$ (lean de-NO_x) reaction on Pt/SiO_2 and Pt/La–Ce–Mn–O catalysts, J. Phys. Chem. B 108 (2004) 2620–2630.

[9] C.N. Costa, A.M. Efstathiou, Mechanistic aspects of the H_2-SCR of NO on a novel $Pt/MgO–CeO_2$ catalyst, J. Phys. Chem. C 111 (2007) 3010–3020.

[10] A.M. Efstathiou, C.N. Costa, J.L.G. Fierro, Catalyst for the reduction of NO to N_2 with hydrogen under NO_x oxidation conditions, US Patent 7,105,137 B2 (2006).

[11] J.A.Z. Pieterse, H. Top, F. Vollink, K. Hoving, R.W. van den Brink, Selective catalytic reduction of NO_x in real exhaust gas of gas engines using unburned gas: catalyst deactivation and advances toward long-term stability, Chem. Eng. J. 120 (2006) 17–23.

[12] R. Burch, J.P. Breen, F.C. Meunier, A review of the selective reduction of NO_x with hydrocarbons under lean-burn conditions with non-zeolitic oxide and platinum group metal catalysts, Appl. Catal. B 39 (2002) 283–303.

[13] M.W. Roberts, The formation of N_2O during the chemisorptions of nitric oxide at platinum surfaces at low temperature: a comment on the mechanism, Catal. Lett. 93 (2004) 29–30.

[14] R. Burch, M.D. Coleman, An investigation of the $NO/H_2/O_2$ reaction on noble-metal catalysts at low temperatures under lean-burn conditions, Appl. Catal. B 23 (1999) 115–121.

[15] C.N. Costa, P.G. Savva, C. Andronikou, P.S. Lambrou, K. Polychronopoulou, V.C. Belessi, V.N. Stathopoulos, P.J. Pomonis, A.M. Efstathiou, An investigation of the $NO/H_2/O_2$ (lean de-NO_x) reaction on a highly active and selective $Pt/La_{0.7}Sr_{0.2}Ce_{0.1}FeO_3$ catalyst at low temperatures, J. Catal. 209 (2002) 456–471.

[16] S. Kikuyama, I. Matsukuma, R. Kikuchi, K. Sasaki, K. Eguchi, A role of components in $Pt–ZrO_2/Al_2O_3$ as a sorbent for removal of NO and NO_2, Appl. Catal. A 226 (2002) 23–30.

[17] N. Macleod, R.M. Lambert, Lean NO_x reduction with $CO+H_2$ mixtures over Pt/Al_2O_3 and Pd/Al_2O_3 catalysts, Appl. Catal. B 35 (2002) 269–279.

[18] V. Pitchon, A. Fritz, The relation between surface state and reactivity in the deNO_x mechanism on platinum-based catalysts, J. Catal. 186 (1999) 64–74.