# Influence of $CO_2$ on storage and release of $NO_x$ on barium-containing catalyst

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A barium-containing three-way automotive emission catalyst was submitted to a $NO_x$ storage step in flowing lean gas mixture containing 340 ppm NO and 8 vol% $O_2$ in helium. $NO_x$ release was carried out in the 250–550 °C temperature range, either in pure helium or in the presence of a 10 vol% $CO_2$ in helium mixture. It was shown that at 450–550 °C all of the stored $NO_x$ on the barium trap can be released fastly in the $CO_2$-containing gas mixture or, after a longer time, in pure helium: these data show that $NO_x$ release can occur in the absence of a reducing agent. The $NO_x$ release was not complete at 350 °C and did not occur at 250 °C. The assisting effect of $CO_2$ as regards to $NO_x$ release was interpreted in terms of the existence of the $CO_{2,\text{gas}} + {*}NO_{2,\text{stored}} \rightleftharpoons {*}CO_{2,\text{stored}} + NO_{2,\text{gas}}$ equilibrium, suggesting the competitive storage of $CO_2$ and $NO_2$ for a unique type of barium storage sites ($*$).

**Keywords:** lean burn, $NO_x$ storage release catalyst, $CO_2$ effect, barium trap

## 1. Introduction

Three-way catalyst (TWC) development has allowed one to limit the emission of nitrogen oxide, carbon oxide and residual hydrocarbons. The optimal running of these catalysts requires an air to fuel ratio of the gas feed near stoichiometry. This leads other kinds of catalysts to be designed to reach a nitrogen oxide conversion in lean conditions [1–8]. Various studies were recently carried out on catalysts presenting a permanent nitrogen oxide conversion such as copper ion exchanged zeolites [9] which unfortunately display a limited catalytic activity and a strong deactivation. More recently, a new type of post-combustion catalysts called "$NO_x$ storage catalysts" were tested [1,4]. They can store, release, and subsequently reduce nitrogen oxides and consist of a nitrogen oxide trap (barium oxide for example) associated with a TWC. They work with lean condition periods separated by rich spikes. In lean conditions, nitrogen oxides are stored over the trap, while hydrocarbons and carbon monoxide are oxidized on noble metal. Takahashi et al. [4] suggested that nitrogen monoxide is first oxidized to $NO_2$ on platinum and then trapped on barium oxide to form a barium nitrate. In rich conditions, nitrogen oxides would be released and reduced to nitrogen by the reducing agent.

In this work, we more particularly took into account the fact that exhaust gases also contain $CO_2$ resulting from hydrocarbon combustion. This paper is devoted to the study of the beneficial and competiting effect of $CO_2$ on the nitrogen oxide storage and release over a "$NO_x$ storage catalyst".

## 2. Experimental

### 2.1. Material

The catalyst used in this work was a "$NO_x$ storage catalyst" supplied by PSA (Peugeot Société Anonyme). It contained platinum and rhodium dispersed on a wash-coat deposited on cordierite and consisted in alumina containing ceria and barium (about 5% in weight). This monolithic catalyst was crushed and sieved according to the method preconized by Salin et al. [10] to get a powder representative of the whole washcoat supported on the monolith.

Before each experiment, samples were pretreated in pure hydrogen (99.995%) for 1 h at 450 °C.

The samples were characterized by X-ray diffraction using a Siemens D500 automatic diffractometer, before and after hydrogen pretreatment. The K$\alpha$ wavelength of copper was selected by a graphite diffracted beam monochromator. Data were collected and analyzed with Sochabim diffract-AT software.

### 2.2. Storage and release experimental methods

Storage and release experiments were carried out on the catalytic setup already described by Fajardie et al. [11]. The reactor was first swept with pure helium (99.995%) for half an hour. $NO_x$ storage was carried out in lean conditions with the gas mixture **1** (340 ppm NO (99%), 8 vol% $O_2$ (99.998%) in helium (99.995%)) corresponding to a lean gas mixture. Nitrogen oxides were detected at the outlet of the reactor with a specific detector using a chemiluminescent analyzer Thermo Electron model 10.

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$NO_x$ release experiments were realized by substituting the gas mixture **1** by either pure helium or a new gas mixture **2** containing 10 vol% $CO_2$ in helium, representative of the $CO_2$ content in the gas exhaust in both lean and rich conditions. $NO_x$ evolutions were followed at outlet of the reactor making possible the study of the influence of helium and carbon dioxide on the release of nitrogen oxide from the barium-trap component.

## 3. Results

### 3.1. Sample characterization

Catalysts were studied by XRD before and after pretreatment by $H_2$ at 350 and 450 °C. The patterns reported in figure 1 mainly evidence the diffraction peaks corresponding to alumina, ceria and cordierite. For the fresh sample and the sample pretreated in $H_2$ at 350 °C, a barium carbonate phase can be identified, which decomposes by $H_2$ pretreatment at a higher temperature (450 °C). No peaks originating from the barium carbonate or any other Ba compounds can be observed. It seems likely that the compounds formed by the possible decomposition of the barium carbonate correspond to amorphous barium oxides or to a higher dispersed oxide on the alumina support, and cannot be evidenced by XRD. Let us note that no X-ray lines of Pt(0) and Rh(0) can be detected by XRD.

### 3.2. Study of $NO_x$ storage and release

Figures 2 and 3 show the different curves of nitrogen oxides storage and release versus time of run at 550 °C, a temperature corresponding to a fast release of stored $NO_x$.

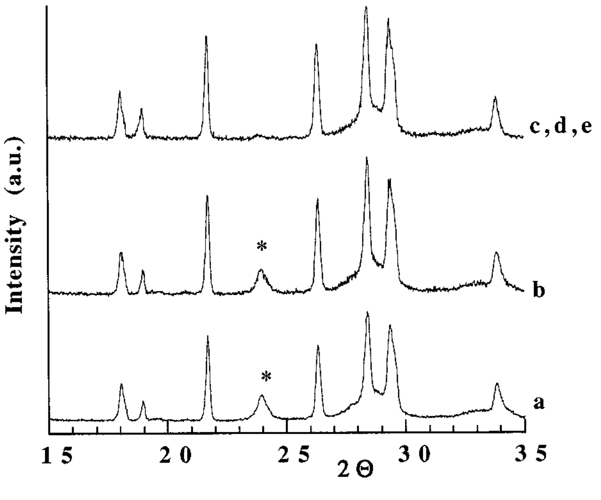

Figure 1. X-ray diffraction pattern of the catalyst: (a) before pretreatment; (b) after pretreatment at 350 °C in flowing hydrogen; (c) after pretreatment at 450 °C in flowing hydrogen; (d) after pretreatment at 350 °C in flowing hydrogen and $NO_x$ storage (340 ppm of $NO_x$, 8 vol% $O_2$ in He) at the same temperature; and (e) after pretreatment at 450 °C in flowing hydrogen and $NO_x$ storage (340 ppm of $NO_x$, 8 vol% $O_2$ in He) at 250, 350 and 450 °C.

### 3.2.1. $NO_x$ storage study

The curve reported in figure 2 refers to the storage of nitrogen oxides at 550 °C on the catalyst, by flowing the gas mixture **1** (340 ppm NO, 8 vol% $O_2$ in He). On this curve, two domains can be distinguished. The $\alpha$-domain represents the initial NO concentration in the gas mixture **1** before contacting the catalyst, whereas the $\beta$-domain shows the evolution of NO concentration in the gas phase versus time of run when the gas mixture flows through the catalyst: first, the nitrogen oxide concentration strongly decreases, then slowly increases up to 340 ppm. It corresponds to the storage of nitrogen oxide by the barium oxide trap and its progressive saturation by nitrogen oxide. The specific interaction of $NO_x$ with the barium trap of the catalyst was evidenced by the disappearance of the XRD peaks of the initial barium carbonate (figure 1) previously identified by the X-ray diffraction pattern of the sample reduced at 350 °C.

### 3.2.2. $NO_x$ release study

*$NO_x$ release at 550 °C.* Figure 3 presents the different $NO_x$ release plots versus time of run carried out at 550 °C, on the preceding $NO_x$-saturated catalyst sample first submitted for 500 s to gas mixture **1**. The $NO_x$ release was in a first step studied by flowing only pure helium as a carrier gas (curve (1), figure 3(a)). It can be seen that $NO_x$ release takes place relatively slowly from 15 s up to 100 s time of run with of maximum at 25 s (peak curve (1)). The surface area of the peak permits to determine the amount of $NO_x$ molecules released at 550 °C by flowing helium alone; it is slightly lower than the amount of the $NO_x$ previously stored (table 1). After this first $NO_x$ release in flowing pure helium, a second $NO_x$ release on the same sample was proceeded by flowing 10 vol% $CO_2$ in helium (gas mixture **2**). This second $NO_x$ release (peak curve (2), figure 3(a)) is obviously smaller (about five times less than that released in helium) but the rate of release is faster than in pure He since it is occurring exclusively between 15 and 40 s. Moreover, the sum of the two amounts of $NO_x$ released in He alone

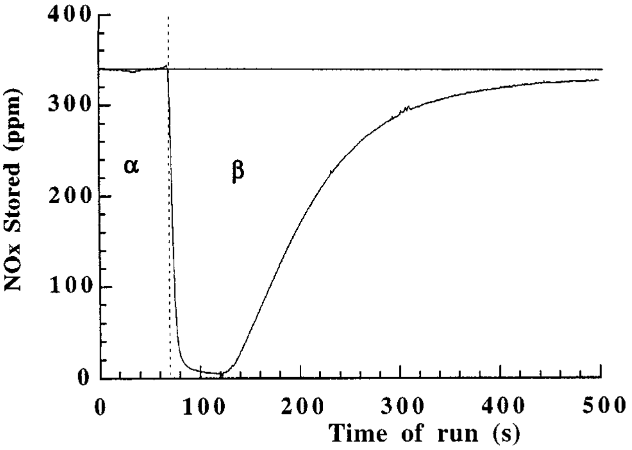

Figure 2. $NO_x$ storage capacity at 550 °C versus time of run: $\alpha$-domain – before storage; $\beta$-domain – during storage.

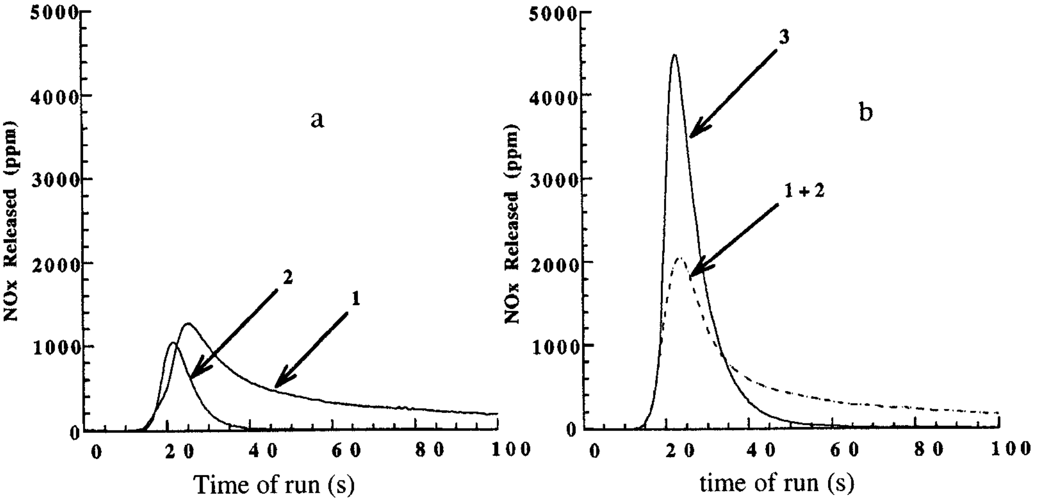

Figure 3. NO$_x$ release at 550 °C versus time of run: (a) in two steps: in flowing helium (curve (1)), then in 10 vol% CO$_2$ in helium (curve (2)); (b) in one step: by flowing 10 vol% CO$_2$ in helium (curve (3)). For a sake of comparison with curve (3), curve (1 + 2) is plotted and represents the total amount of NO$_x$ released in two steps.

Table 1
Amounts of NO$_x$ stored and released (in moles per gram of catalyst) as a function of temperature and carrier gas composition during the releasing step.

| Temperature (°C) | No$_x$ amount stored (mol/g-cat) | Two-step No$_x$ release (mol/g-cat) | | | One-step NO$_x$ release, 10 vol% CO$_2$ in He (mol/g-cat) |
|---|---|---|---|---|---|
| | | He | 10 vol% CO$_2$ in He | Total amount | |
| 250 | 198 | – | – | – | – |
| 350 | 164 | 37 | 43 | 80 | 82 |
| 450 | 100 | 55 | 39 | 94 | 93 |
| 550 | 37 | 33 | 6 | 39 | 36 |

(first step), then in CO$_2$ in helium (second step), fairly corresponds to the total amount of NO$_x$ previously stored on the sample, taking into account the amount released in the tail of the helium plots.

Using the gas mixture **1**, a new NO$_x$ storage was subsequently done on the same preceding sample, just regenerated by the CO$_2$-containing gas mixture **2**. After this second saturation of the barium trap by NO, a one-step NO$_x$ release by flowing gas mixture **2** was carried out. A narrow peak (see curve (3), figure 3(b)) can be observed, similar to the preceding peak (curve (2), figure 3(a)), but with a higher intensity, and a surface area corresponding to the total amount of previously stored nitrogen oxide (table 1, columns 2 and 6). So, it has been shown that at 550 °C, all the NO$_x$ stored on the catalyst can be released fastly by flowing a 10 vol% CO$_2$ in helium mixture evidencing the beneficial effect of CO$_2$ in the process. A longer time is required to release this total NO$_x$ amount by flowing pure helium.

As a conclusion, carbon dioxide is able to release nitrogen oxides more fastly than helium.

*NO$_x$ release in the 250–550 °C temperature range.* Similar experiments were conducted at different temperatures between 250 and 550 °C. The amounts of nitrogen oxides stored and released for each temperature were evaluated and are presented in table 1. It appears that: (i) the total amount of stored NO molecules decreases when the temperature increases, (ii) for each temperature, the nitrogen dioxide amounts released in the two steps – first in helium alone, then in 10 vol% CO$_2$ in helium (see sum 1 + 2 in figure 3(b)) – still remain equal to those released in one-step experiments (10 vol% CO$_2$ in helium, figure 3(b)). In the 450–550 °C temperature range all the NO$_x$ previously stored can be considered as completely released from the trap by flowing 10% of CO$_2$ in He (see table 1, columns 2 and 6). At 350 °C the stored NO$_x$ can be only partially released. At 250 °C, no nitrogen oxide release was observed. It was verified by thermodesorption carried out between 250 and 550 °C under pure helium or under 10 vol% CO$_2$ in helium (figure 4) that NO$_x$ previously stored on the catalyst at 250 °C, started to desorb at 300 °C with a maximum of desorption at 400 °C in both cases. However, let us note again that in flowing helium the desorption is not complete at 550 °C, whereas it is complete at 450 °C in the presence of CO$_2$. So, it can be concluded that the release of stored NO$_x$ in a one-step process can be complete at a temperature higher than 350 °C in the presence of CO$_2$, and that it is possible to store again the same quantity of NO$_x$ in a second subsequent experiment.

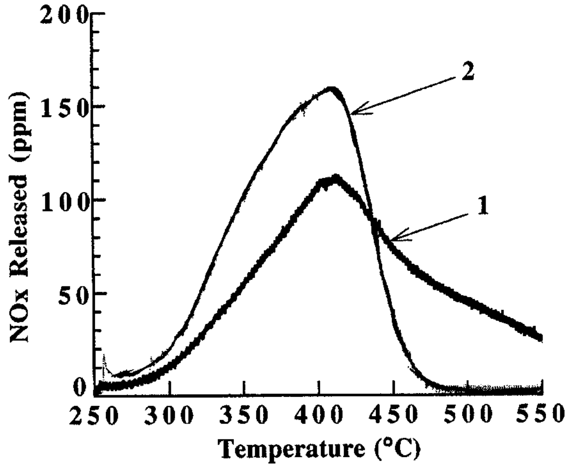

Figure 4. $NO_x$ release versus temperature (temperature-programmed experiments): in flowing helium (curve (1)) and in flowing 10 vol% $CO_2$ in helium (curve (2)).

## 4. Discussion

Already published studies on "$NO_x$ storage catalysts" always considered $NO_x$ release in the presence of a reducing agent [1–8]. To make mass spectroscopy analysis of the exhaust gases easier, authors have generally used hydrogen as the reductor. Furthermore, in all cases they have not taken into account the effect of $CO_2$ (originating from fuel combustion and from oxidation of CO in real gas exhaust) on $NO_x$ release.

We have evidenced in this work that a total $NO_x$ release could be achieved in the presence of a gas mixture containing $CO_2$ and in the absence of any reducing agents. This work also shows that stored nitrogen oxides could be partially released in pure helium at 300 °C by a simple thermal treatment; after addition of 10 vol% $CO_2$ in the helium flow, $NO_x$ release becomes complete at 450 °C.

So, it seems likely that the $NO_x$ release phenomenon is assisted by the presence of $CO_2$ and that the presence of a reducing agent is not a necessary condition for its occurrence.

Referring to the preceding results, we can notice that the releasing rate of nitrogen oxides is a function of both temperature and releasing mixture composition. With helium, the releasing rate is slower than with 10 vol% $CO_2$ in helium. With pure helium the releasing peak displays an extensive tail, increasing as the temperature decreases. In the presence of carbon dioxide, the $NO_x$ release is always faster, as shown by the curve profiles, with a limited spreading over effect.

These data confirm, once again, the existence of an "assisting effect" of carbon dioxide on $NO_x$ release. A global mechanism can be proposed as shown in figure 5.

By thermal treatment under hydrogen at 450 °C, the barium carbonate contained in the untreated sample decomposes and in contact with mixture **1**, stores nitrogen oxides, as $NO_{2,\mathrm{stored}}$ entities on its surface, in agreement with previous works [1,4]. Equilibrium (1) can be expected on the barium trap ("Ba") surface between ($NO_{2,\mathrm{stored}}$) on the barium storage sites (∗) and the $NO_2$ molecules in the gas phase. When the $NO_x$ release is realized by flowing pure helium the $NO_2$ gas elimination occurs, which displaces equilibrium (1) in the direction of the release of $NO_{2,\mathrm{stored}}$ entities. The release phenomenon is kinetically slow and probably needs high temperatures to be complete.

$$*NO_{2,\mathrm{stored}} \rightleftharpoons NO_{2,\mathrm{gas}} \qquad (1)$$

When $CO_2$ is introduced in the releasing mixture, it competes with $NO_{2,\mathrm{gas}}$ to interact with the same storage sites on

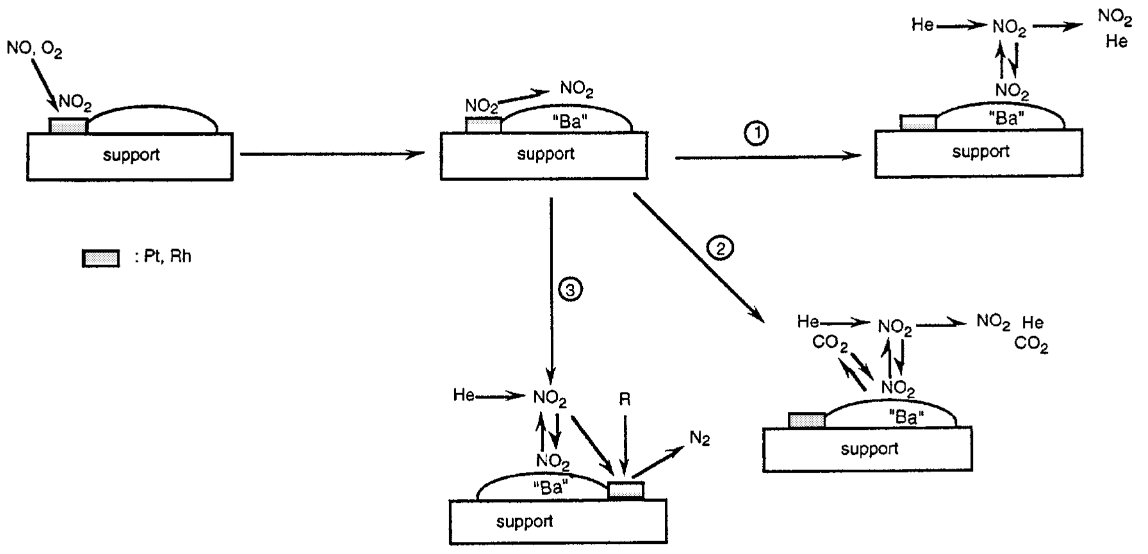

Figure 5. General scheme for the $NO_x$ storage and release process over a barium compound supported on TWC. Pt,Rh/support mainly corresponds to the TWC functions: oxidation of NO to $NO_2$ in lean burn conditions, reduction of NO to $N_2$ in rich conditions. (1) $NO_2$ release from Ba compounds in rich conditions; (2) competitive effect of $CO_2$ on NO storage and release; (3) $NO_2$ release and reduction in the presence of a reducing agent such as CO or any hydrocarbons.

the barium oxide trap. A new equilibrium (equilibrium (2)) can then be assumed which shows how $CO_2$ can promote the rapid release of $NO_x$ molecules fixed on the barium oxide sites, by displacing equibrium (2), in the direction of the formation of $NO_{2,\mathrm{gas}}$ molecules. It has been evidenced that the elimination of $NO_x$ can be completely achieved in these conditions. The existence of equilibrium (2) necessarily involves the limitation of the $NO_x$ storage, by addition of $CO_2$ in gas mixture **1**. Such a $CO_2$ effect on $NO_x$ storage has been effectively verified.

$$CO_{2,\mathrm{gas}} + {*NO_{2,\mathrm{stored}}} \rightleftharpoons {*CO_{2,\mathrm{stored}}} + NO_{2,\mathrm{gas}} \qquad (2)$$

In the presence of a simple reducing agent such as pure hydrogen, two reactions both occur simultaneously: (i) $NO_x$ release by molecular $H_2$, according to a similar releasing effect as that proposed for pure helium, with a concomitant diffusion of $NO_{\mathrm{gas}}$ in the gas phase towards the metallic sites Pt(0), Rh(0) of the three-way catalyst, (ii) $NO_2$ reduction by hydrogen dissociated on these metallic sites into nitrogen and water. In this work we assumed that the surface barium sites on which $NO_2$ stores are not too far from the metallic sites. In these conditions the $NO_{2,\mathrm{gas}}$ diffusion step cannot be rate determining, which can explain the fairly high apparent rate of releasing of $NO_2$ observed. In fact, the $NO_{\mathrm{gas}}$ molecules will be consumed via their reduction by $H_2$ on the metal, which so displaces the preceding equilibrium in the direction of the $NO_2$ releasing.

## 5. Conclusions

A barium-containing three-way automotive was studied. This catalyst was able to carry out $NO_x$ storage in lean conditions, and $NO_x$ release and reduction in rich conditions. In this work we studied the effect of $CO_2$ and helium on $NO_x$ release. We have shown that $NO_x$ release in helium can start at 300 °C, and that $CO_2$ added in helium increases the $NO_x$ releasing rate, which leads to focus attention on the assisting effect of this gas as regards to $NO_x$ release.

This work evidences the existence of the $NO_{2,\mathrm{stored}} \rightleftharpoons NO_{2,\mathrm{gas}}$ equilibrium on the barium coumpound surface, which was proved by the study of the influence of $CO_2$ on the direction of its displacement. This equilibrium appeared to be determining for $NO_x$ releasing. We have proved that: (i) $NO_x$ release was possible in the presence of pure helium alone, which consequently demonstrated that the presence of a reducing agent was not indispensable to release $NO_x$, in contrast with previous author assumptions [1,4–7], (ii) the introduction of $CO_2$ in helium displaced the $NO_{2,\mathrm{ads}} \rightleftharpoons NO_{2,\mathrm{gas}}$ equilibrium and increased the $NO_x$ release rate, which evidenced the competitive storage of $CO_2$ and $NO_2$ for the same barium sites.

Finally, the present work, by studying the influence of $CO_2$ and He on the nitrogen oxides release, affords specific informations on the $NO_x$ releasing phenomenon. In contrast, previous works on $NO_x$ release carried out in the presence of reducing agents only accounted for the global contribution of the release reduction of $NO_x$.

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## References

[1] N. Miyoshi, M. Matsumoto, K. Katoh, T. Tanaka, J. Harada, N. Takahashi, K. Yokota, M. Sugiura and K. Kasahara, SAE Technical Paper Series 950809 (1995).

[2] T. Kobayashi, T. Yamada and K. Kayano, SAE Technical Paper Series 970745 (1997) 63.

[3] M.S. Brogan, R.J. Brisley, J.S. Moore and A.D. Clarck, SAE Technical Paper Series 962045 (1996) 43.

[4] F. Takahashi, H. Shinjoh, T. Iijima, T. Susuki, K. Yamazaki, K. Yokota, H. Suzuki, M. Miyoshi, S. Matsumoto, T. Tanizawa, T. Tanaka, S. Tateishi and K. Kasahara, Catal. Today 27 (1996) 63.

[5] S. Matsumoto, Catal. Surv. 1 (1997) 111.

[6] A. Schmoltz and W. Böegner, Int. J. Hydrogen Energy 18 (1993) 433.

[7] W. Bögner, M. Krämer, B. Krutzch, S. Pischinger, D. Voitländer, G. Venninger, F. Wirbeleit, M.S. Brogan, R.J. Brisley and D.E. Webster, Appl. Catal. B 7 (1995) 153 F.

[8] E. Fridell, M. Skoglundh, S. Johansson, B. Westerberg, A. Torncrona and G. Smedler, CAPOC IV, Stud. Surf. Sci. Catal. 116 (1998) 537.

[9] S. Sato, Y. Yu, H. Yahiro, N. Mizuno and M. Iwamoto, Appl. Catal. 70 (1991) L1.

[10] S. Salin, C. Potvin, J.-F. Tempère, M. Boudart and G. Djéga-Mariadassou, Ind. Eng. Chem. Res. 37 (1998) 4531.

[11] F. Fajardie, J.F. Tempère, J.M. Manoli, O. Touret, G. Blanchard and G. Djéga-Mariadassou, J. Catal. 179 (1998) 469.