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The mechanism for NO_x storage

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The mechanisms for storing of NO_x in platinum–barium–alumina catalysts during lean–rich transients are investigated. Oxidation of NO to NO_2 is found to be an important step. NO_2 is found to be important for oxidation of the catalyst or of nitrites to form nitrates. NO_x is then stored in the form of surface nitrates. FTIR studies show no formation of bulk nitrates in these experiments.

Keywords: lean burn, nitrogen oxides, NO_x storage catalyst, platinum, barium, NO_2, surface nitrates

It is essential to reduce the emissions into the atmosphere of the greenhouse gas CO_2 from fossil sources [1]. Since traffic is a major source it is important to find ways to improve the fuel economy of cars. One way to contribute to this is to replace the normal petrol engines, running at stoichiometric conditions, with lean burn engines. However, this leads to the problem of reducing nitrogen oxides in the lean exhaust emitted by these engines. The three-way catalysts used today are not able to do this and, therefore, new catalytic systems are needed. So-called selective catalytic reduction using ammonia as reducing agent, seems to work relatively well [2]. There is, however, great resistance to implement this kind of solution, where a separate tank with ammonia or urea solution is needed in the vehicle. Continuous reduction with hydrocarbons as the reducing agent is therefore more attractive but has not yet proven to give large enough conversions to solve the problems with NO_x emissions even though several different types of catalysts have been investigated [3,4].

A different way to solve this problem is to use a so-called NO_x storage catalyst in combination with mixed lean operation of the engine. In this case, NO_x is trapped in the catalyst under lean conditions. As the catalyst becomes saturated with NO_x it needs to be regenerated. This is achieved by tuning the engine to rich conditions for a short period so that the stored NO_x is released and reduced to N_2. These types of systems are sold by Toyota for the Japanese market [5]. The main obstacle for introduction in Europe is presently the relatively high level of sulphur in gasoline. Sulphur will bind to the catalyst in the form of sulphates and deactivate the NO_x storage function [6,7]. However, it is possible to produce low sulphur gasoline and a stricter future legislation is expected in Europe opening up for NO_x storage systems to be implemented.[1]

This letter deals with the mechanisms for storage of NO_x. In order to investigate this more closely it is useful to simplify the system. The essential functions of the catalyst are (1) oxidation of hydrocarbons and NO, (2) storage of NO_x and (3) release and reduction of stored NO_x under rich conditions. The model samples we have used contain Pt for oxidation and reduction, barium as storage compound and alumina as support material. Some experiments on samples without either Pt or Ba have also been performed for comparison. Simplified gas mixtures with oxygen, NO_x and reducing agents were used.

Monolith samples with 2 wt% Pt and 20 wt% BaO in the washcoat were prepared by wet deposition methods as described in [8].

Most experiments were performed in a flow reactor system, described elsewhere [9], equipped with a chemiluminescence detector for NO and NO_2 and IR instruments for CO_2 and N_2O. In order to mimic the mixed lean conditions, transient experiments where the gas mixture is regularly altered between lean and rich conditions have been performed. Normally this was achieved by turning on and off the oxygen in the gas flow and replacing it with inert gas. Typically the gas mixture then contains O_2, NO, C_3H_6 and inert gas under lean conditions and NO, C_3H_6 and inert gas for the rich period. However, several variations on this have also been used. An important parameter is the amount of NO_x that is stored in each lean period. This amount is obtained from the NO_x signal measured after the catalyst during the transients as described in [8].

The first step in the NO_x storage sequence is the oxidation of NO to NO_2 taking place on Pt sites. The kinetics for this over supported Pt have been studied by Olsson et al. [10] and it is found that the rate-limiting step is the reaction between NO and adsorbed atomic oxygen. Figure 1 shows the NO_2 signal after the NO_x storage catalyst during a heating ramp in a lean gas mixture containing 600 ppm NO, 900 ppm C_3H_6 and 8% O_2. At low temperatures NO_2 is favoured over NO from thermodynamic considera-

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[1] Low levels of sulphur originating from lubricants will still slowly deactivate the catalyst. It is therefore essential to find suitable sulphur regeneration strategies for these systems.

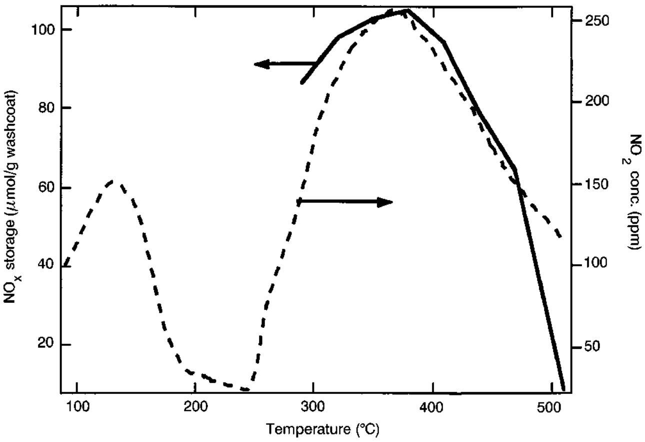

Figure 1. The amount NO_x stored in the $Pt/BaO/Al_2O_3$ catalyst during one lean period (of 240 s) in lean–rich transients (- - -) as a function of catalyst temperature. Also shown is the NO_2 concentration during a heating ramp in a lean gas mixture (—). Gas mixtures: lean – 600 ppm NO, 900 ppm C_3H_6, 8% O_2; rich – 600 ppm NO, 900 ppm C_3H_6; SV 54000 h^{-1}; heating rate 5 °C min^{-1}.

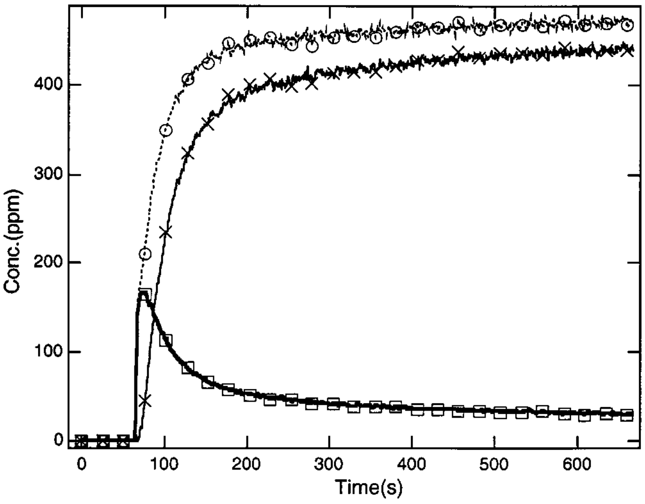

Figure 2. The NO (□), NO_2 (×) and NO_x (○) signals upon adsorption of NO_2 on the NO_x storage catalyst at 400 °C.

tions [10] and the oxidation of NO is kinetically limited. At the temperatures around 250 °C one can observe selective reduction of NO (to N_2O and N_2) by propene. In the temperature range above 380 °C the NO_2 concentration follows the thermodynamic equilibrium values. Also shown in figure 1 is the NO_x storage yield during one lean period measured in lean–rich transients. The two curves follow each other fairly closely in the temperature range 300–500 °C. At $T > 500$ °C the storage yield drops more quickly than the NO_2 concentration, indicating that the species formed during the NO_x storage process are unstable at these temperatures.

Figure 2 shows the NO, NO_2 and NO_x ($NO_x = NO + NO_2$) signals when the NO_x storage catalyst is exposed to 500 ppm NO_2 in Ar at a space velocity of 110000 h^{-1} and a temperature of 400 °C. An initial formation of NO can be observed indicating that the sample is oxidised by

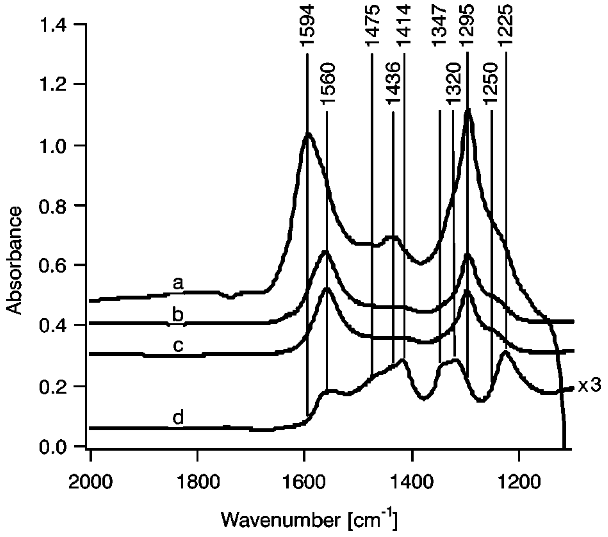

Figure 3. IR spectra of $Pt/BaO/Al_2O_3$ exposed to: (a) NO_2 and O_2 during 8 min at 150 °C; (b) NO_2 and O_2 during 8 min at 300 °C; (c) NO and O_2 during 8 min at 300 °C; and (d) NO and O_2 during 8 min at 150 °C. Curve (d) is magnified by a factor of three.

NO_2. Similar measurements on a BaO/Al_2O_3 sample reveal the same behaviour while a Pt/Al_2O_3 sample does not show any sign of being oxidised in the same manner. This shows that it is the barium part of the sample that is oxidised. This observation may be attributed to two different mechanisms. Either the barium surface itself is oxidised. This could then involve the formation of barium peroxide, BaO_2, which has earlier been identified for similar systems [11] and may be formed from oxidation by NO_2 [12]. Thermodynamically, the formation of BaO_2 from barium and oxygen is favourable up to 600 °C. Alternatively, NO_2 may form nitrites on the surface of barium which in turn are oxidised to nitrates by NO_2 in a reaction where NO desorbs into the gas phase.

The actual storing takes place via formation of nitrites and, mainly, nitrates. In the lean–rich cycles, supposed to mimic the mixed lean conditions, only a fraction of the available barium is used as storage sites [8]. From this observation it is reasonable to assume that the formed nitrates persist on the surface of Ba and this is indeed supported by the IR measurements. Figure 3 shows the IR spectra when the NO_x storage catalyst is exposed to mixtures of either NO and O_2 or NO_2 and O_2 at temperatures of 150 and 300 °C. Both nitrates and nitrites can be observed in the spectra. In mixtures of NO and O_2 at 150 °C (curve (d)), the formation of surface nitrites is observed as peaks at 1225 and 1320 cm^{-1} for bridged nitrite, peaks at 1347 and 1436 cm^{-1} for monodentate nitrite, a peak at 1475 cm^{-1} for linear nitrite and a peak at 1414 cm^{-1} for N-coordinated nitrite [13–16]. At 300 °C (curve (c)) and in mixtures of NO_2 and O_2 (curves (a) and (b)) mainly nitrates are observed with peaks at 1250 and 1594 cm^{-1} for bidentate nitrates and peaks at 1295 and 1560 cm^{-1} for monodentate nitrates [13–16]. The assignments and features of the FTIR spectra will be further discussed in a future publication [17].

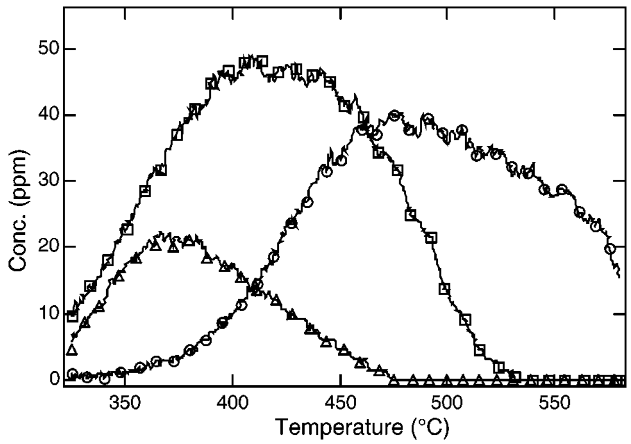

Figure 4. NO$_x$ desorption vs. temperature after NO$_2$ adsorption at 300 °C for the Pt/BaO/Al$_2$O$_3$ (□), the Pt/Al$_2$O$_3$ (△) and the BaO/Al$_2$O$_3$ (○) samples.

For the case of NO and O$_2$ at 150 °C the formation of nitrites rather than nitrates is connected to the low concentrations of NO$_2$ for this case [10]. One important observation from figure 3 is that no formation of bulk nitrates can be observed for any case, indicated by the absence of a band due to free nitrate ions at around 1380 cm^{-1} [15,16].

For an effective regeneration of the NO$_x$ storage catalyst from NO$_x$, the presence of Pt and a reducing agent are required. NO$_x$ may also thermally desorb from the surface in the form of NO or NO$_2$. Figure 4 shows the desorption of nitrogen oxides in an inert flow after adsorption of NO$_2$ at 300 °C for the Pt/BaO/Al$_2$O$_3$, Pt/Al$_2$O$_3$ and BaO/Al$_2$O$_3$ samples, respectively. For the NO$_x$ storage catalyst there is a maximum around 420 °C. Much less NO$_x$ is seen to desorb from the Pt/Al$_2$O$_3$ sample with a maximum at 375 °C. For the BaO/Al$_2$O$_3$ sample, the NO$_x$ desorption maximum is observed at higher temperatures compared with the NO$_x$ storage catalyst. For a sample with Pt, the desorption temperature is about 100 K lower than for a BaO/Al$_2$O$_3$ sample. When a reducing agent is present, the regeneration is much more rapid resulting in the production of N$_2$ and N$_2$O rather than NO$_x$ [8]. For a sample without Pt, regeneration with, e.g., C$_3$H$_6$ is not possible [8].

Figure 5 shows the response (NO, NO$_2$, N$_2$O and CO$_2$) at 400 °C during transients with 5 min of NO$_2$ followed by 5 min of NO$_2$ + C$_3$H$_6$, for three different samples: Pt/BaO/Al$_2$O$_3$ (the NO$_x$ storage catalyst), Pt/Al$_2$O$_3$ and BaO/Al$_2$O$_3$. According to the mechanism outlined above, NO$_x$ storage–regeneration cycles should be observable in these transients. Since NO$_x$ is in the form of NO$_2$, the first step, NO oxidation, has already been achieved. The oxidation of the barium surface or the nitrites is achieved by the strong oxidising agent NO$_2$. The NO$_2$ can then form nitrates on the surface as observed by FTIR [8,17].

Regarding NO$_x$ storage, this is clearly seen for these cycles for the Pt/BaO/Al$_2$O$_3$ sample. There is a slow increase in the NO$_x$ signal for the NO$_2$-only period and a significant CO$_2$ peak at the beginning of the rich period when the stored NO$_x$ is reduced. Observe the high formation of NO in the beginning of the NO$_2$-only period, indicating that oxygen from NO$_2$ is bound in the sample leaving NO to desorb as discussed above. The NO and NO$_2$ concentrations then level out to their steady-state values. The Pt/Al$_2$O$_3$ sample shows only very little – if any – NO$_x$ storage. The BaO/Al$_2$O$_3$ sample shows only little storage, manifested in a NO desorption for the NO$_2$ + C$_3$H$_6$ period. However, when increasing the temperature to 500 °C, some storing can actually be observed for the BaO/Al$_2$O$_3$ sample. The reason may be that although the catalyst cannot be re-

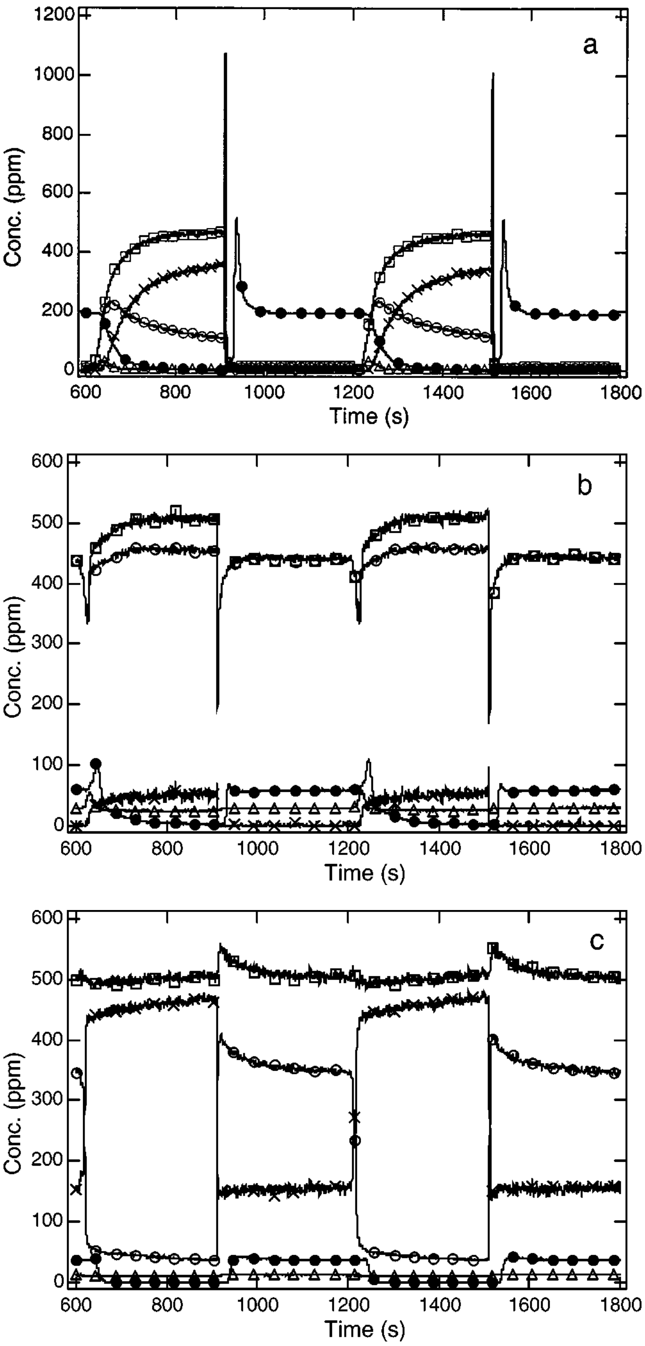

Figure 5. The NO (○), NO$_2$ (×), NO$_x$ (□), N$_2$O (△) and CO$_2$ (●) signals for lean–rich cycles at 400 °C. Lean mixture: 500 ppm NO$_2$, 5 min; rich mixture: 500 ppm NO$_2$, 1000 ppm C$_3$H$_6$, 5 min. (a) Pt/BaO/Al$_2$O$_3$, (b) Pt/Al$_2$O$_3$ and (c) BaO/Al$_2$O$_3$.

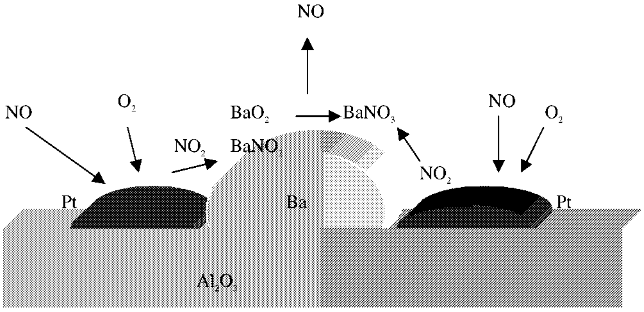

Figure 6. A schematic view of the NO_x storage sequence.

generated by propene because of the lack of noble metals, the stored NO_x may thermally desorb at this temperature as was seen in figure 4 above.

Several different observations can be made from figure 5. First, one may note that the relative abundance of NO and NO_2, with only NO_2 in the feed gas, vary between the samples. As expected, the samples containing Pt push the concentrations further towards NO (closer to the thermal equilibrium) than the samples without Pt (the latter show almost no dissociation of NO_2 to NO). However, the Pt/Al_2O_3 sample is much more active than the $Pt/BaO/Al_2O_3$ sample in this respect. The reason for this is probably connected with electron donation from barium oxide to Pt. This influence of BaO on the catalytic properties of Pt has earlier been observed for n-butane combustion [18]. During the periods with NO_2 and propene, all NO_2 is reduced to N_2, H_2O and CO_2 for the (NO_x storage) $Pt/BaO/Al_2O_3$ sample. A large CO_2 peak can be seen initially for this sample. The Pt/Al_2O_3 sample, on the other hand, only reduces about 10% of the NO_x under these conditions. The rest leaves the catalyst in the form of NO. The reason for this poor reduction capability is most likely that the Pt sites become self-poisoned by propene (or propene derived species). Interestingly, this poisoning does not take place when barium is present. The Pt-free samples do not reduce NO_x but partly reduce NO_2 to NO. There is a CO_2 peak when turning off the propene for the Pt/Al_2O_3 sample. This can be attributed to oxidation, by NO_2, of stored HC when the poisoning of the Pt sites disappears.

The sequence for NO_x storage is illustrated in figure 6. In summary it is found that NO oxidation and activation of the NO_x storage sites, possibly by the formation of barium peroxides, are important steps prior to the formation of surface barium nitrates in the NO_x storage catalysts. Only the presence of NO_2 is required to effectively store NO_x in a model NO_x storage sample. It is found that the sample is activated by oxygen from NO_2 to be able to store NO_x. This stored NO_x can then be regenerated by C_3H_6. It seems as if a BaO/Al_2O_3 sample cannot be regenerated by C_3H_6, but regeneration from thermal desorption can be observed at higher temperatures.

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