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The removal of NO_x from a lean exhaust gas using storage and reduction on $H_3PW_{12}O_{40}\cdot 6H_2O$

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Abstract

NO_x sorption and reduction capacities of 12-tungstophosphoric acid hexahydrate ($H_3PW_{12}O_{40}\cdot 6H_2O$, HPW) were measured under representative alternating conditions of lean and rich exhaust-type gas mixture. Under lean conditions, the sorption of NO_x is large and is equivalent to 37 mg of NO_x/g_{HPW}. Although a part of these NO_x remains unreduced, HPW is able to reduce some of the NO_x to produce N_2 by a reaction between the sorbed NO_2 and hydrocarbon (HC), but this process is slow. The addition of 1% Pt affects strongly the chemical behaviour occurring during the course of a rich operation. The NO desorption observed at the beginning of the rich phase is strongly accelerated. The direct correlation between NO_2 consumption and CO_2 production shows that the principal pathway is the reaction $CO + NO_2 \rightarrow CO_2 + NO$. In a mixture of reducing gas (CO, HC, H_2), the competition is strongly in favour of CO though in its absence the reaction observed was the hydrogenation of propene to propane. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: NO_x sorption; Lean exhaust gas; Selective catalytic reduction

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1. Introduction

A decrease in the consumption of fuel by gasoline engines is, particularly in respect of CO_2 emissions, a crucial parameter in the reduction of contributions towards the greenhouse effect. For this reason, the development of lean engines operating under excess air conditions has been initiated by the car industry. These types of engine, in which the excess air conditions result in lower CO_2 emissions, are far more fuel-efficient than their gasoline equivalents which operate at a stoichiometric air/fuel ratio. However, despite the generally low engine exhaust emission level of lean engines under excess air, there is a significant contribution to air pollution, particularly with respect to NO_x which present a major environmental and health hazard since they are involved, by their reaction with unburned hydrocarbons (HCs), in the formation of smog and earth level ozone [1]. Research to develop an appropriate after-treatment system comparable with TWC is currently underway. Unfortunately, the most promising NO_x reduction scheme suitable for the lean engine is based on selective catalytic reduction (SCR), which exhibits limited efficiency and is not yet in commercial production [2,3]. Therefore, alternative techniques including a step of NO_x storage are being given consideration. A concept recently emerged is based on the use of an NO_x storage and reduction catalyst (NSR) [4,5]. In this technology, the nitrogen oxides are stored on the catalyst during the lean cycle and are subsequently reduced to harmless nitrogen during the rich or stoichiometric operation.

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Most of these systems contain inorganic oxides [6], mixed oxides [7,8], or modified three-way catalysts [9] though they present the disadvantage of sorbing mainly NO_2 while only a very small fraction of NO is trapped [10,11]. Recently, we have presented the results of a new type of absorbent, namely the heteropolyacids from the Keggin family and among them the 12-tungstophosphoric acid hexahydrate ($H_3PW_{12}O_{40}\cdot 6H_2O$, HPW) [12]. This catalyst has some remarkable features including an absorption capacity which is very high when compared with that obtained on barium systems. Equally, a co-absorption of NO and NO_2 in an equimolar ratio is observed which is in contrast to other oxide systems. This arises because the NO_x are trapped in the form of an N_2O_3 intermediate rather than the $NO_3{}^-$ form obtained on the classical Pt/Ba doped catalysts [13]. Also, desorption is possible according to two different procedures: the first by heating and the second by cooling in wet air, this latter method being completely reversible and reproducible [14]. An exchange of NO and NO_2 with the structural water molecules of the secondary Keggin's structure has been shown to occur during cooling. Finally, a prolonged stability with respect to time was recorded (>50 h), no deactivation was observed when the catalyst use was maintained at 170 °C. Until now these formulations have not been tested under alternating conditions of lean and rich exhaust gas composition. Therefore, the focus of this paper is the evaluation of an optimised lean-burn catalyst by the detailed study of the various reactions which can occur during rich operation on HPW and Pt doped HPW.

2. Experimental

The catalytic material was purchased from Strem Chemicals and was characterised by XRD following a period of 3 h in an oven at 110 °C before reaction. This pre-heating procedure ensures the stoichiometry of $6H_2O$ for the HPW and a good crystallisation of the solid. The addition of 1% of platinum was made by impregnation of an H_2PtCl_6 solution. The solid was then dried overnight in an oven at 110 °C. The atomic absorption analysis showed that chlorine is removed from the sample during the first experiment due to the presence of water.

The experimental setup, designed in the laboratory, is a full computer driven system. The experiments were conducted in a flow reactor using a series of mass flow controllers by alternating simulated rich and lean gas compositions with different times of excursion. The two gas compositions were used in a simulation of either a lean-burn or rich exhaust and their components are presented in Table 1. The uptake and desorption capacity of NO/NO_2 were measured isothermally using a furnace and a temperature controller with a mass of catalyst of 330 mg and a flow of 300 cm^3/min. Water was removed from the stream via a permeation tube prior to the recording of NO and NO_2 concentrations by means of a Rosemount-type analyser with an accuracy of ±10 ppm. Punctual N_2O analysis confirmed the exclusion of this species from both the gas flow and during the test sequence. The amount of NO_x trapped, reduced or desorbed was calculated by integration of the curves of both NO and NO_2 for sorption and reduction, respectively, and expressed as milligram of NO_2 per gram of catalyst. The analysis of propene, propane, N_2O and CO_2 was performed by means of online rapid chromatography.

In a real engine the rich period does not exceed a few seconds but for the case under study it was prolonged over 20 min, in order to study in detail both gas composition and reaction rates at steady state, which yields essential information concerning the reaction mechanism.

Table 1
Synthetic gas composition simulating lean-burn or rich exhaust (N_2 balance)

Exhaust	NO (ppm)	NO_2 (ppm)	C_3H_6 (ppm)	O_2 (%)	CO (%)	H_2 (%)	H_2O (%)	CO_2 (%)
Lean	500	500	–	10	–	–	5	5
Rich	–	–	600	0.5	3	1	10	10

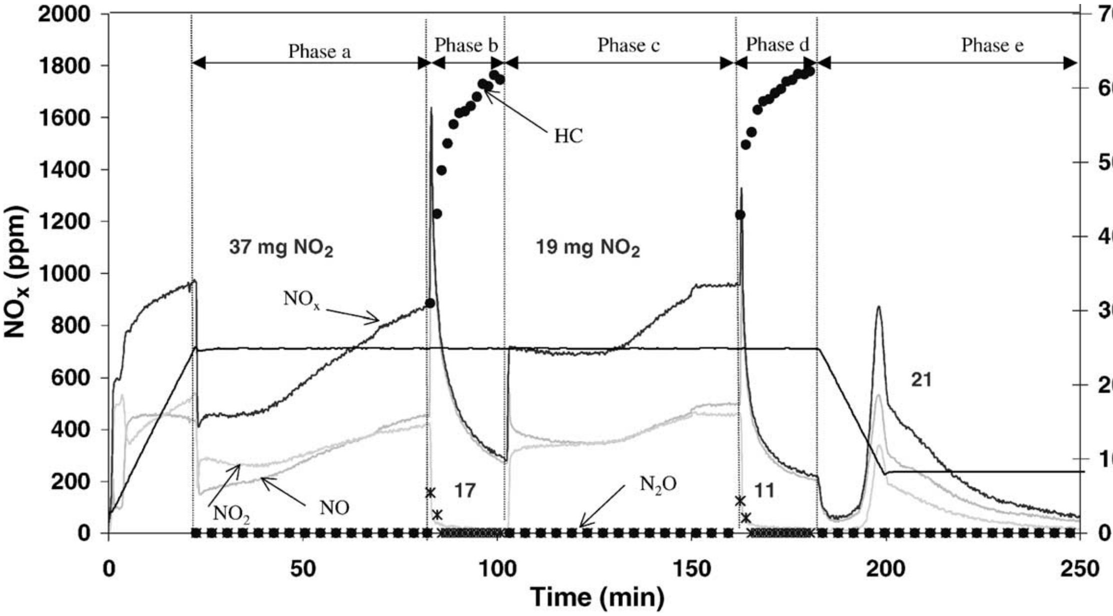


Fig. 1. HPW behaviour at 250 °C under two cycles of lean/rich excursion and a phase of desorption by cooling: 500 ppm NO, 500 ppm NO_2, 10% O_2, 5% H_2O, 5% CO_2 (phases ‘a’ and ‘c’); 600 ppm HC, 3% CO, 1% H_2, 0.5% O_2, 10% H_2O, 10% CO_2 (phases ‘b’ and ‘d’); cooling under 5% H_2O in air (phase ‘e’).

3. Results and discussion

3.1. HPW

In Fig. 1 the various treatments of HPW are presented. These were carried out by imposing two successive phases of lean sorption/rich reduction followed by a single phase of desorption by cooling in wet air (5% H_2O). The sorption and reduction were performed at 250 °C. This temperature was chosen because it is within the range of practical application and also the performances of the catalyst are good. In this experiment the presence of CO_2 in large concentration (5%) throughout the test rendered its analysis impossible. For the first lean/rich cycle the gas stream, previously in the by-pass circuit, was directed to the reactor when both NO_x concentration (1000 ppm) and the temperature were stable. During the first run (phase ‘a’), NO and NO_2 were slowly co-absorbed in equimolar quantity leading to a value of 37 mg of NO_x/g_{HPW}. This process occurs via a substitution of the water molecules by NO_x to form an $[H^+(NO_2^-, NO^+)]$ complex. A bulk phenomenon unrelated to the surface, the amount of NO_x adsorbed corresponds to a complete, i.e. stoichiometric, substitution of water, whereby six molecules of water are replaced by three (NO^+, NO_2^-). The gas mixture was then switched to the rich composition at 250 °C for 20 min (phase ‘b’) and immediately a sharp peak of pure NO is registered. The reduction then proceeded over 20 min resulting in 17 mg of NO_2 being reduced to N_2 or desorbed as NO (phase ‘b’). During a second run under lean conditions the uptake proved equal to 19 mg of NO_2 per gram of HPW (phase ‘c’), while only 11 mg of NO_2 were reduced (phase ‘d’). This revealed a deactivation which, due to an accumulation of carbonaceous deposits, increased over the sequence of runs (not shown) [15]. The final step, cooling in wet air, permitted the desorption of 21 mg of remaining unreduced NO_x (phase ‘e’) and arising from the replacement of the NO_x by water molecules to reform secondary Keggin’s structure.

The reduction phase ‘b’ and the peculiar desorption which occurred at the beginning of this phase is more clearly presented on the enlargement (Fig. 2). The evolution of NO_x, NO, NO_2 and C_3H_6 with time, reveals that the appearance of the peak in NO

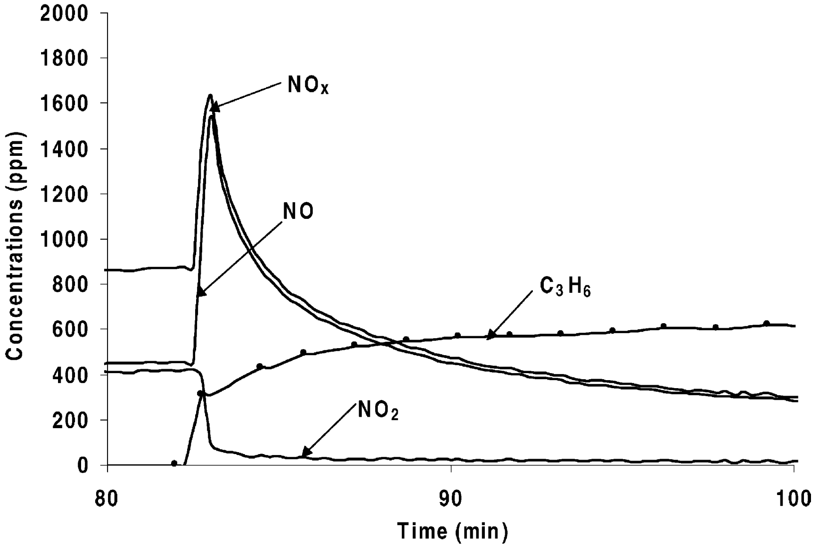


Fig. 2. Detailed gas analysis of a rich phase with 600 ppm HC, 3% CO, 1% H_2, 0.5% O_2, 10% H_2O and 10% CO_2 at 250 °C on HPW.

concentration, for which the maximum attained is ca. 1600 ppm, is associated with both a sharp decrease in the concentration of NO_2 simultaneous with a marked slowing in the increase of propene concentration. This observation of the parallel consumption of NO_2 and C_3H_6, along with the deactivation discussed previously, suggests a major role for propene.

Fig. 3 confirms the potential importance of the presence of propene as the sole active agent of the gas mixture. In this different experiment the reduction phase contains 3% CO, 1% H_2, 0.5% O_2 and 10% H_2O. During the lean phase (not shown) the same value for absorption, i.e. 37 mg of NO_x/g_{HPW} was measured. In this case, however, the overshooting peak following the switch to rich is no longer observed. Also remarkable is the absence of CO_2 which, since it was not present as a reactant, could have been analysed here. Finally, the quantity of unreduced $NO+NO_2$ obtained by cooling (not shown) is high and equal to 33 mg of NO_x/g_{HPW} rather than 20 as in the presence of HC.

Several attempts were made to trap products believed to be formed during the reduction using selective trapping on Tenax and Carbosieve columns followed by heating and GC–MS analysis. This methodology revealed only very small concentrations of secondary products [15] which implies that they are probably not intermediates of the reaction between NO_2 and C_3H_6 whose final product nitrogen is formed by the transformation, on the HPW, of the major intermediate. Unfortunately, the complementary gas being N_2, its detection is therefore impossible. Nevertheless, the information can be obtained indirectly by the analysis of NO_2, NO and C_3H_6 which are indeed analysed. From Fig. 1, only 7 mg of NO_2 are not refound from the NO_x balance and correspond to the amount probably transformed in N_2. We propose therefore that there is a fast reaction according to Scheme 1, between the double bond of C_3H_6 and NO_2 rapid enough to yield a mixture of dinitro products which at this temperature could easily be transformed into N_2 [16].

The dinitro species implies a stoichiometry between propene and NO_2 equal to 1/2. The propene is oxidised into CO_2 and H_2O.

The formation of NO in the breakthrough peak could either be issued from the desorption of the pre-absorbed NO or from the partial reduction of NO_2 by the following reaction:

$$C_3H_6 + 9NO_2 \rightarrow 9NO + 3CO_2 + 3H_2O$$

This possibility is not excluded since it would concern a small quantity of C_3H_6 as it is indeed observed, the only restriction being the very fast rate of the reaction observed.

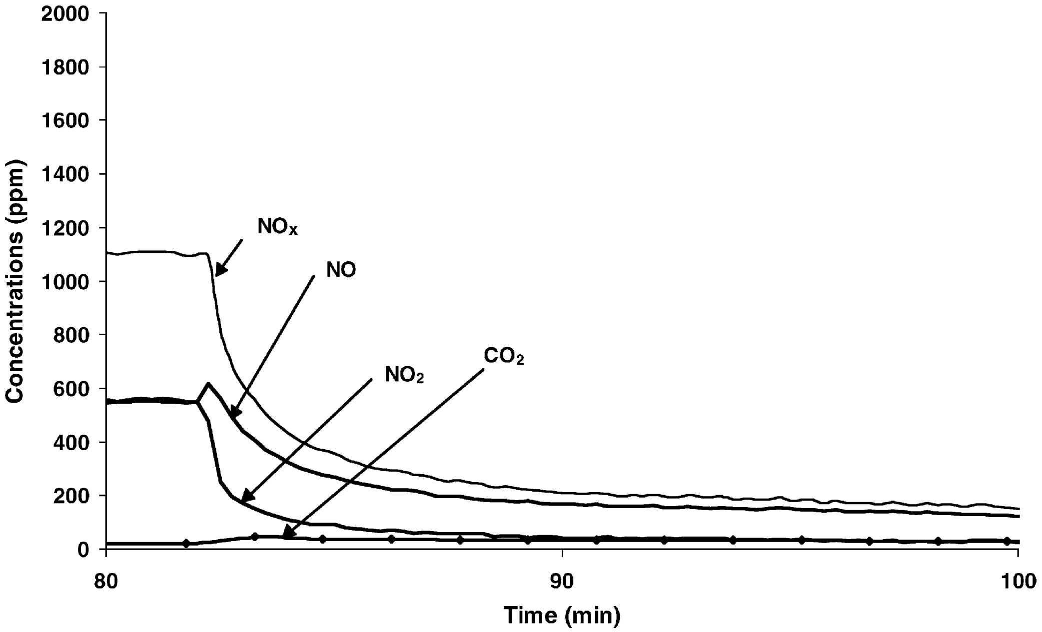
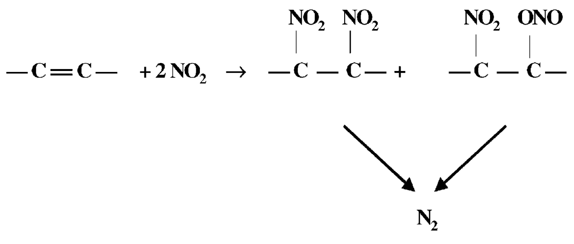


Fig. 3. Detailed gas analysis of a rich phase without HC and CO_2, and with 3% CO, 1% H_2, 0.5% O_2 and 10% H_2O at 250 °C on HPW.

3.2. 1% Pt/HPW

The same operating procedure was applied to the solid 1% Pt/HPW at 250 °C and the sequence is presented in Fig. 4. The behaviour during both the sorption and reduction phases is very different. In this experiment, the sorption is faster than with HPW, producing a sharper peak (phase ‘a’). The amount of NO_2 stored is equal to 26 mg/g_{HPW}. The addition of platinum favours the efficiency resulting in a sharper peak, probably due to an adsorption of NO_x on platinum sites. During the rich phase, only a small reduction was observed and the NO + NO_2 desorbed exclusively as pure NO within less than 3 min (phase ‘b’) giving rise to a sharp peak on the analyser which overshot the range of analysis. During the second run, the uptake is of 19 mg (phase ‘d’). This value reveals that there is a small deterioration in the sorption capacity between the first and the second runs but following this period of stabilisation no more deactivation was observed as the number of runs increased (not shown). The fact that all of the NO_x are desorbed or reduced during the rich step is confirmed by the absence of NO_x during the cooling desorption in wet air (phase ‘e’). Also worth noting is the fact that the deactivation is a lot less important in the presence of Pt.



$$-\mathrm{C}{=}\mathrm{C}- \quad +2\,\mathrm{NO_2} \rightarrow -\overset{\overset{\mathrm{NO_2}}{|}}{\mathrm{C}}-\overset{\overset{\mathrm{NO_2}}{|}}{\mathrm{C}}- + \quad -\overset{\overset{\mathrm{NO_2}}{|}}{\mathrm{C}}-\overset{\overset{\mathrm{ONO}}{|}}{\mathrm{C}}- \quad \searrow \swarrow \; \mathrm{N_2}$$

Scheme 1.

A detailed analysis of the phenomena occurring during the rich phase is presented in Fig. 5. In contrast to HPW without Pt, the propene consumption is low and the return to the initial value of 600 ppm is almost immediate. This behaviour could account for the absence of deactivation by carbonaceous deposit as discussed previously. Clearly, the role of HC is not as important in the presence of Pt. In order to discover the possible action of the other reducing agents, complementary experiments were carried out. Fig. 6 shows the first of these in which the rich phase contains only 3% CO. A comparison of the profile obtained under standard rich conditions (Fig. 5) with Fig. 6, reveals great similarity. In the final case, with the analysis of

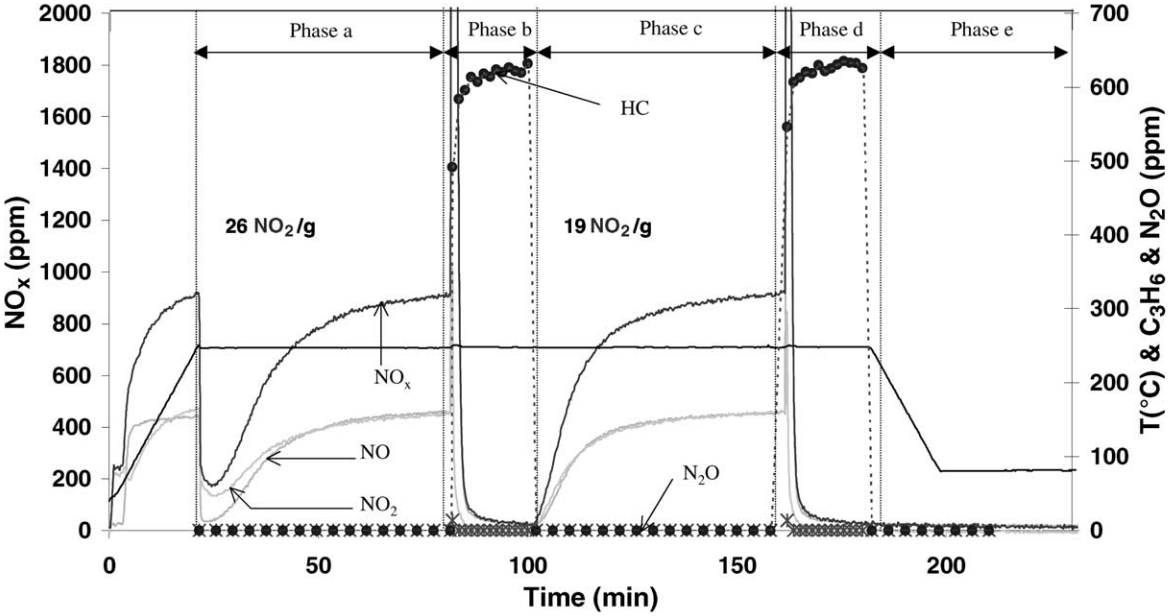


Fig. 4. Pt/HPW behaviour at 250 °C under two cycles of lean/rich excursion and a phase of desorption by cooling: 500 ppm NO, 500 ppm NO_2, 10% O_2, 5% H_2O, 5% CO_2 (phases 'a' and 'c'); 600 ppm HC, 3% CO, 1% H_2, 0.5% O_2, 10% H_2O, 10% CO_2 (phases 'b' and 'd'); cooling under 5% H_2O in air (phase 'e').

CO_2 possible, its formation is abundant and related to both NO production and NO_2 consumption. Since CO_2 is not obtained in the absence of Pt, the reaction which occurs is therefore different. On Pt/HPW, the main reaction pathway corresponds to [17]

$$CO + NO_2 \rightarrow CO_2 + NO$$

Nevertheless, a careful examination of Fig. 6, reveals that the reaction time is slower than that obtained with the standard gas mixture (Fig. 5), the peak of NO being much broader in the absence of HC and H_2, implying a possible role for these two reductants. In an attempt to determine this role, a rich phase without CO was tested, the experiment is presented in Fig. 7. In this case, the rich mixture contains 600 ppm HC, 1% H_2 and 0.5% O_2; several observations can be made.

- At steady state all the propene is hydrogenated to propane; this the only case in which propane was obtained with this catalyst, suggesting that platinum ensures the dissociation of hydrogen yet only in the absence of CO. In the presence of CO, the competition for the adsorption sites between CO and H_2 is strongly in favour of CO and following the principal reaction between CO and NO_2, when all the NO_x are removed from their sorption sites, the reaction remaining is $CO + (1/2)O_2 \rightarrow CO_2$.
- There is no CO_2 formation, which confirms the point above and proves that there is no reaction between HC and O_2, but only between HC and H_2.
- At the beginning of the reduction, there is a small overshooting peak of NO correlating with the consumption of HC and decrease of NO_2. This behaviour is the same as that observed with HPW when not impregnated with Pt. Also, the presence of a peak of apparently unaffected NO_x when cooling (not shown), the time required for the NO desorption and the absence of a return to the baseline for NO concentration clearly demonstrates that the reduction capacity is affected. Thus, in the presence of Pt, CO is a much more efficient reductant than HC.

To summarise, the impregnation of Pt on HPW facilitates the adsorption of CO and consequently

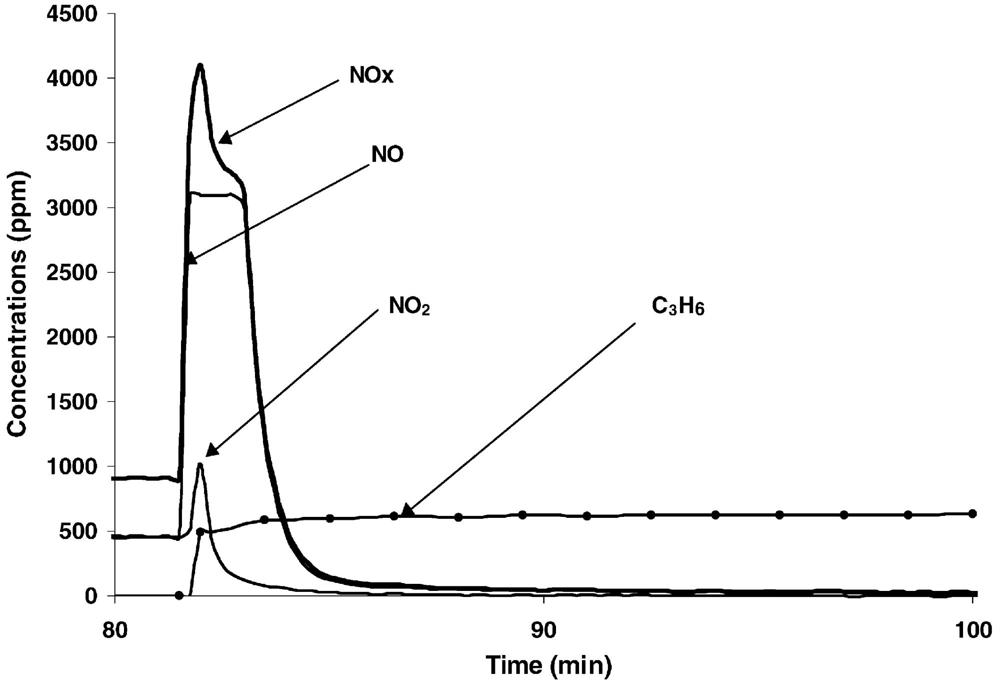


Fig. 5. Detailed gas analysis of a rich phase with 600 ppm HC, 3% CO, 1% H_2, 0.5% O_2, 10% H_2O and 10% CO_2 at 250 °C on Pt/HPW.

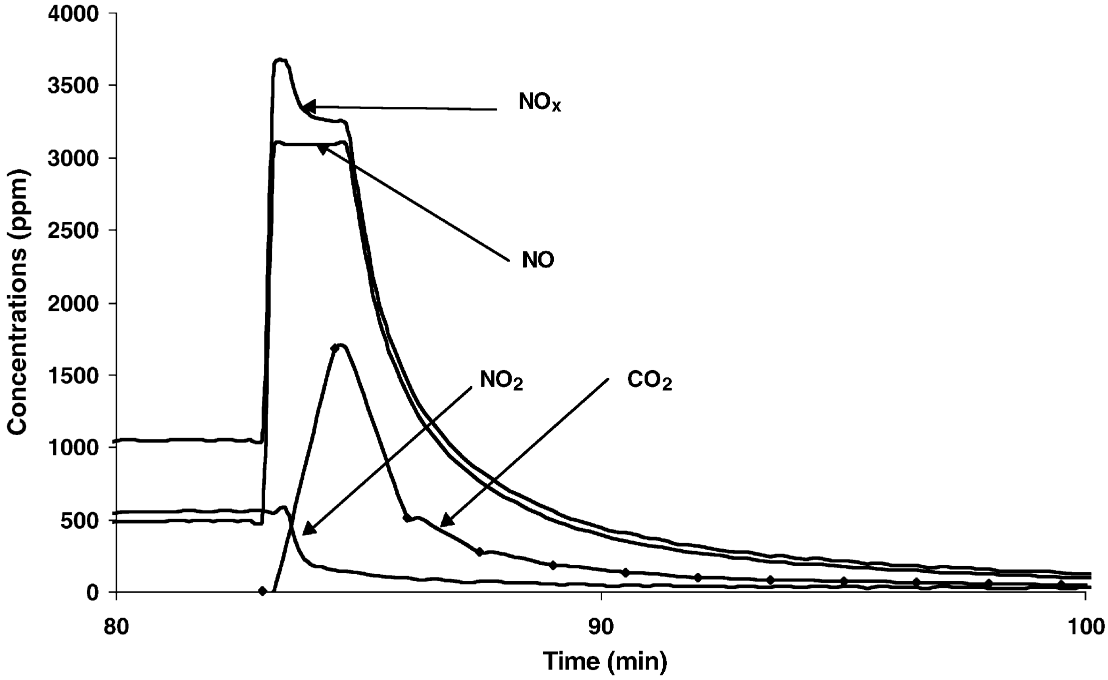


Fig. 6. Detailed gas analysis of a rich phase with 3% CO and 10% H_2O at 250 °C on Pt/HPW.

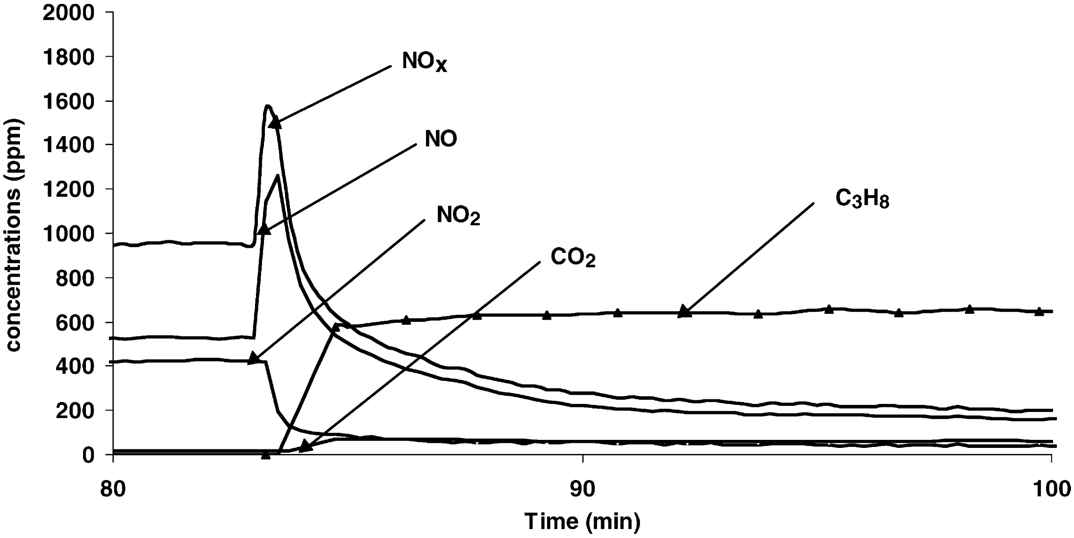


Fig. 7. Detailed gas analysis of a rich phase with 600 ppm C_3H_6, 1% H_2, 0.5% O_2 and 10% H_2O at 250 °C on Pt/HPW.

improves its reducing character. The rapidity of the reaction between NO_2 and CO inhibits that between C_3H_6 and NO_2 observed with non-impregnated HPW.

4. Conclusion

In a previous work we have reported the great capacity of a new class of sorbent, namely the heteropolyacids, in particular $H_3PW_{12}O_{40}\cdot 6H_2O$, to trap selectively both NO and NO_2 in a lean exhaust gas [12]. The aim of this research was to evaluate the potential of such a system in a lean/rich operation, to check out its resistance to a strongly reducing atmosphere and to verify if the reduction of the trapped NO_x was possible during a rich excursion.

The work undertaken has clearly demonstrated that the HPW structure does not deteriorate when exposed to a rich mixture of gas. After a lean phase at 250 °C, a large amount of NO_x is trapped. The trapping ability is the result of the co-absorption of NO and NO_2 and is independent of the presence of platinum. However, the behaviour of NO and NO_2 towards reduction upon rich exposure is quite different. Although a fraction of these gases is directly reduced into nitrogen, the majority of NO desorbs unreduced. The nitrogen probably results from the rearrangement of a dinitro intermediate formed by a reaction of C_3H_6 with NO_2.

As this reaction is not fast enough for an engine application, 1% of platinum was introduced. This addition affected strongly the chemical behaviour occurring during the course of a rich operation. In this case, the phenomenon of NO desorption at the beginning of the rich phase is strongly accelerated and apparently no longer related to HC but rather to CO. The direct correlation between NO_2 consumption and CO_2 production leads to the conclusion that the principal pathway comprises the reaction $CO + NO_2 \rightarrow CO_2 + NO$. In a mixture of reducing gas (CO, HC, H_2), the competition is strongly in favour of CO though in its absence the reaction observed was the hydrogenation of propene to propane.

Therefore, these experiments have led us to the findings that while Pt/HPW is a very good system for NO_x trapping in a lean environment the reduction is not achieved and only the desorption of NO is possible which is not the aim of the lean/rich technology. We have therefore developed a dual-bed technique through which a reduction is accomplished by a three-way catalyst located on a bed placed after the sorbent. With this methodology an overall reduction of at least 90% was obtained [18].

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