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Removal of NO_x from a Lean Exhaust Gas by Absorption on Heteropolyacids: Reversible Sorption of Nitrogen Oxides in $H_3PW_{12}O_{40} \cdot 6H_2O$

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NO_x adsorption/desorption capacities of 12-tungstophosphoric acid hexahydrate (HPW) were measured under representative exhaust lean gas mixture conditions. The amounts of NO_x adsorbed were large and equal to 38 mg/g of HPW. On such material desorption is observed during the cooling phase under wet air conditions. This type of behaviour is very unusual and has never been reported previously. NO and NO_2 are absorbed and desorbed in an equimolar ratio without nitrate formation. The mechanism of adsorption proceeds by the substitution of lattice water molecules and formation of a $[H^+(NO_2^-, NO^+)]$ complex. During the cooling phase and in the presence of water, around 100°C, reverse substitution occurs. © 2001 Academic Press

Key Words: **NO_x storage; lean burn; tungstophophoric acid.**

1. INTRODUCTION

The elimination of NO_x arising from diesel exhausts presents a major challenge to automotive industries worldwide. Many processes have been conceived, each based upon two different methods: either by the direct reduction of NO to nitrogen on stream or by selective NO_x trapping followed by reduction (1). For the latter, Daimler–Benz have developed a very attractive technique called SNR (selective NO_x recirculation) in which NO_x gases are returned to the combustion chamber where they are reduced by combustion processes following selective sorption (2, 3). SNR technology is made of two parallel NO_x trap beds that alternately adsorb the NO_x produced by the engine or desorbed the stored NO_x for recirculation. A small gas stream, either air or engine exhaust gas, is used to recirculate NO_x into the engine. Generally, a temperature rise is applied to provoke the desorption. The key point in such a device is the efficiency of the sorbent, which should have a high NO_x sorption capacity at low temperature (100–300°C), and the facility to desorb the resultant gases at a little higher temperatures (maximum 550°C). These systems are numerous and are mainly based upon inorganic oxides (4), mixed oxides (5, 6), and well-defined structures such as perovskites (7), cuprates (8) or modified three-way catalysts (9).

The most efficient of these formulations contain barium oxide, which is easily converted to nitrate (10, 11), but they absorb selectively NO_2 and not NO (12). The sorption of NO_x on oxides containing an alkali or an alkali earth element is the most active of those reported in the literature, though they present the major inconvenience of proceeding by a preferential reaction with NO_2 to form a nitrate. The thermodynamic stability of such compounds, i.e., requiring a high temperature for decomposition to occur, limits the practical applications for an SNR process due to the need for high-energy input to reach the temperature of desorption. Hence, there is a requirement for developing sorbents that do not produce nitrates. According to the literature, several families of sorbents possessing this quality might be considered. For example, few oxides (Co_3O_4, CuO, Fe_3O_4, etc.) absorb NO to form nitrosyls or nitrites (13, 14) but their absorption capacities are small. Layered structures such as $La_{2-x}Ba_xSrCu_2O_6$ are able to trap NO in the between layering of CuO (15) yet these structures are not very stable thermally and are strongly deactivated in the presence of O_2. Some Y-type zeolites undergo co-adsorption of NO and NO_2 with the formation of an N_2O_3 complex (16), but only seem to operate at low temperatures. A commercially available, active carbon material (17) or carbon fibres produced by steam activation of coal (ACFs) (18) have shown high NO and NO_2 adsorption capacities through the filling of micropores but their oxidative stability and hence their regenerability limit their application.

In the literature the results of two different teams, reporting the adsorption of nitrogen oxides on 12-tungstophosphoric acid (HPW), a compound of the heteropolyacid family having the formula $H_3PW_{12}O_{40} \cdot 6H_2O$ (19, 20), appeared almost simultaneously. HPW is an ionic solid; its structure comprises primary units called Keggin anions, which are constructed from the arrangement of $12WO_6$

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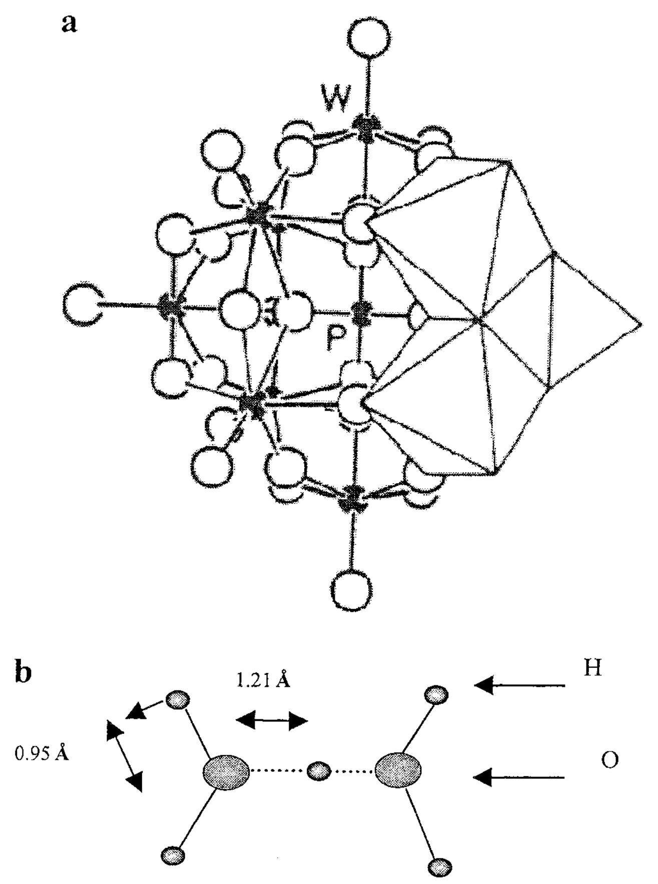

FIG. 1. (a) Representation of the primary Keggin unit of HPW; (b) representation of the $(H_5O_2)^+$ complex.

octahedra about a central tetrahedron, PO_4 (Fig. 1a). The Keggin's polyanions are linked together by $H^+(H_2O)_2$ bridges (Fig. 1b) to form the so-called secondary structure that was fully described in 1977 in *Acta Crystallography* by Brown *et al.* (21).

When considering the systems cited above, HPW appears very attractive yet there remains the necessity to study its behaviour with respect to NO_x absorption under conditions resembling as closely as possible vehicle driving conditions with a real car exhaust mixture containing, for example, CO_2, H_2O, or hydrocarbons. The reports in the literature do not take into account this essential requirement for authenticity and equally their results appear to lead to contradictory conclusions concerning the possible mechanism of absorption. Therefore, our approach has been to use different experimental techniques to produce new evidence permitting the elucidation of the mechanism of both NO_x absorption and desorption on HPW. In this paper, the correlation between the absorption capacity and the structural properties will be described. Also, the influence of a variety of experimental parameters upon the absorption ability will be examined and reported. Finally, a section will be devoted to the mechanistic study of the absorption/desorption process on 12-tungstophosporic acid ($H_3PW_{12}O_{40} \cdot 6H_2O$).

This research has been undertaken as part of a collaborative European project whose partners are Daimler-Chrysler AG and Johnson Matthey from industry along with the Universities of Leuven (COK), Strasbourg (LERCSI), and Gothenburg (Chalmers). One of the principal objectives is the development of a material able to selectively trap NO_x arising from both lean-burn or diesel engines.

2. EXPERIMENTAL

2.1. *Samples*

The catalytic material was purchased from Strem Chemicals and it was characterised by XRD following a period of 3 h in an oven at 110°C before and after reaction. This preheating procedure ensures the stoichiometry of $6H_2O$ for the HPW and good crystallisation of the solid. Indeed, before such pretreatment the structure is very poorly resolved, as observed by XRD, because of the great affinity of HPW for water and is in a pseudoliquid state. In some cases, 1% of platinum was added by impregnation of an H_2PtCl_6 solution. The solid was then dried overnight in an oven.

2.2. *Test Procedure*

2.2.1. Apparatus and gas composition. A gas mixture of NO, NO_2, H_2O, O_2, CO, CO_2, hydrocarbon (C_3H_6), and N_2 with a defined concentration for each gas flows with a velocity of $300\,\mathrm{cm}^3\,\mathrm{min}^{-1}$ through a quartz flow reactor containing the catalyst on a fixed bed. The concentrations of NO and NO_2 were monitored by NO and NO_2 analysers (Rosemount Analytical Binos 4.2) over a range of 0–3000 ppm. Experiments were performed under two sets of conditions, i.e., lean burn and diesel; for each case the detailed composition of the gaseous composition is given in Table 1.

2.2.2. Standard test procedure. The test procedure comprised a stabilisation period, for the complete gas mixture (lean burn or diesel), of 30 min in the bypass. The gas was then allowed to flow through the reactor containing 330 mg of the absorbent preheated to 80°C and stabilised at this temperature for 15 min. The furnace is heated from 80 to 550°C with a ramp rate of 4°C min^{-1}. This procedure

TABLE 1

Gas Composition under Lean Burn and Diesel Conditions

Diesel		Lean Burn	
Gas	Concentration	Gas	Concentration
NO	1,000 ppm	NO	500 ppm
CO	300 ppm	NO_2	500 ppm
CO_2	50,000 ppm	CO_2	50,000 ppm
C_3H_6	50 ppm	C_3H_8	0 ppm
O_2	100,000 ppm	O_2	100,000 ppm
H_2O	50,000 ppm	H_2O	50,000 ppm

was then repeated twice to verify the reproducibility of the experiments. Due to the thermal stability of HPW, the maximum was adapted to both the following of the changes of the structural properties by XRD and the loss of absorption capacity during one experiment. This set of data will be detailed in the Results section. The amount of NO_x trapped and then released upon desorption was estimated by an integration of the curve below or above the baseline (1000 ppm) for absorption or desorption, respectively, and by expression as mg of NO_x/g of HPW. Since both signals of NO and NO_2 are recorded, this value is exact.

2.3. *X-Ray Diffraction*

In some cases, X-ray diffraction was performed with a Siemens D-5000 diffractometer using Cu Kα radiation, with a continuous acquisition between 10° and 90° and a step of 0.02° for ca. 60 min.

2.4. *Fourier Transform Infrared Spectroscopy*

For IR studies, a fraction of the catalyst withdrawn from the reactor following a test was diluted into KBr and pressed in the form of a pellet (diameter 13 mm). The same masses of KBr and sample were used for all the solids and the IR spectra reported result from a prior subtraction of the control. IR spectra were recorded using a Nicolet 5DXC; the spectral domain was between 400 and 4000 cm^{-1} with a 2-cm^{-1} resolution.

2.5. *Thermogravimetric Analysis*

The apparatus was a TG-DTA 92-10 from Setaram coupled with a quadrupole mass spectrometer from Fisons. Acquisition of the data was performed continuously using commercial interface and software. The crucible containing about 100 mg of catalyst was heated to 980°C in air with a ramp rate of 10°C min^{-1} with both heat transitions and mass loss being recorded.

3. RESULTS

3.1. *Absorption/Desorption Capacity under Lean-Burn Conditions*

The first test undertaken was conducted by raising the temperature up to 550°C under a lean-burn mixture following a dwelling period of 15 min at 80°C. This operation was repeated twice. During the first run, absorption of NO_x between 100 and 300°C was observed followed by desorption between 300 and 550°C as described by Fig. 2. The amounts of NO_x absorbed and then desorbed were equal and of 38 mg/g of HPW. For the two subsequent cycles this amount fell dramatically to 4.5 mg/g. The literature reports a thermal fragility of the heteropolyacid structure (22). This structural degradation corresponds to the loss of the $H^+(H_2O)_2$ bridges.

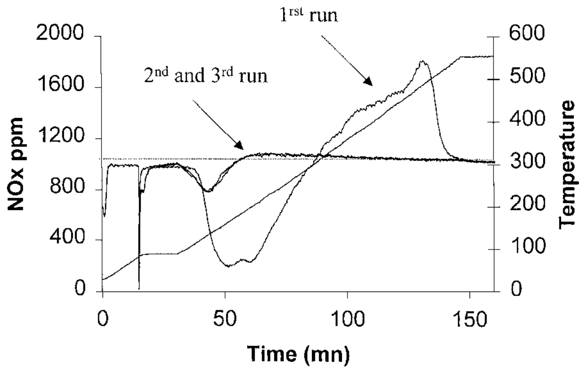

FIG. 2. Adsorption–desorption profile of NO_x with a lean-burn mixture on HPW (three cycles).

To evaluate the limits of stability of the structure of the adsorbent during the desorption phases, several temperatures between 450 and 170°C were attempted. The results of these experiments are given in Figs. 3a–3d. An irregularity was observed in the broad range of temperature tested. The amounts of NO_x absorbed and desorbed thermally were always different. The quantity of NO_x absorbed is always 38 mg g^{-1} while the amount desorbed decreases from 25 mg g^{-1} at 450°C to 16 mg g^{-1} at 400°C and only 6 mg g^{-1} at 350°C. At 170°C, the value is nil (Table 2). This discrepancy is explained by the fact that on such material *desorption is observed during a cooling phase* under wet air (5% water). The peak of desorption is centered around 100°C. In Table 2, the sum of the amounts of NO_x absorbed and then desorbed either thermally or during the cooling phase are reported. If the two modes of desorption are taken into account, then the amount of NO_x desorbed is equal to the amount of NO_x previously absorbed. This type of behaviour is very unusual and has never been reported previously. Also worth noting is the fact that the amount of NO_x desorbed during cooling increases when the corresponding test temperature decreases. This experiment clearly demonstrates that the problem of the thermal stability of HPW observed during high temperature of desorption could be overcome by this new process of cooling desorption.

TABLE 2

Influence of the Temperature of Desorption upon the Amount of NO_x Desorbed during the First Cycle of Adsorption/Desorption

	Temperature (°C)				
	550	450	400	350	170
NO_x adsorbed (mg/g)	38	38	38	38	38
NO_x desorbed while heating (mg/g)	38	30	19	8	0
NO_x desorbed while cooling (mg/g)	0	8	19	30	38
Total of NO_x absorbed/desorbed	38/38	38/38	38/38	38/38	38/38

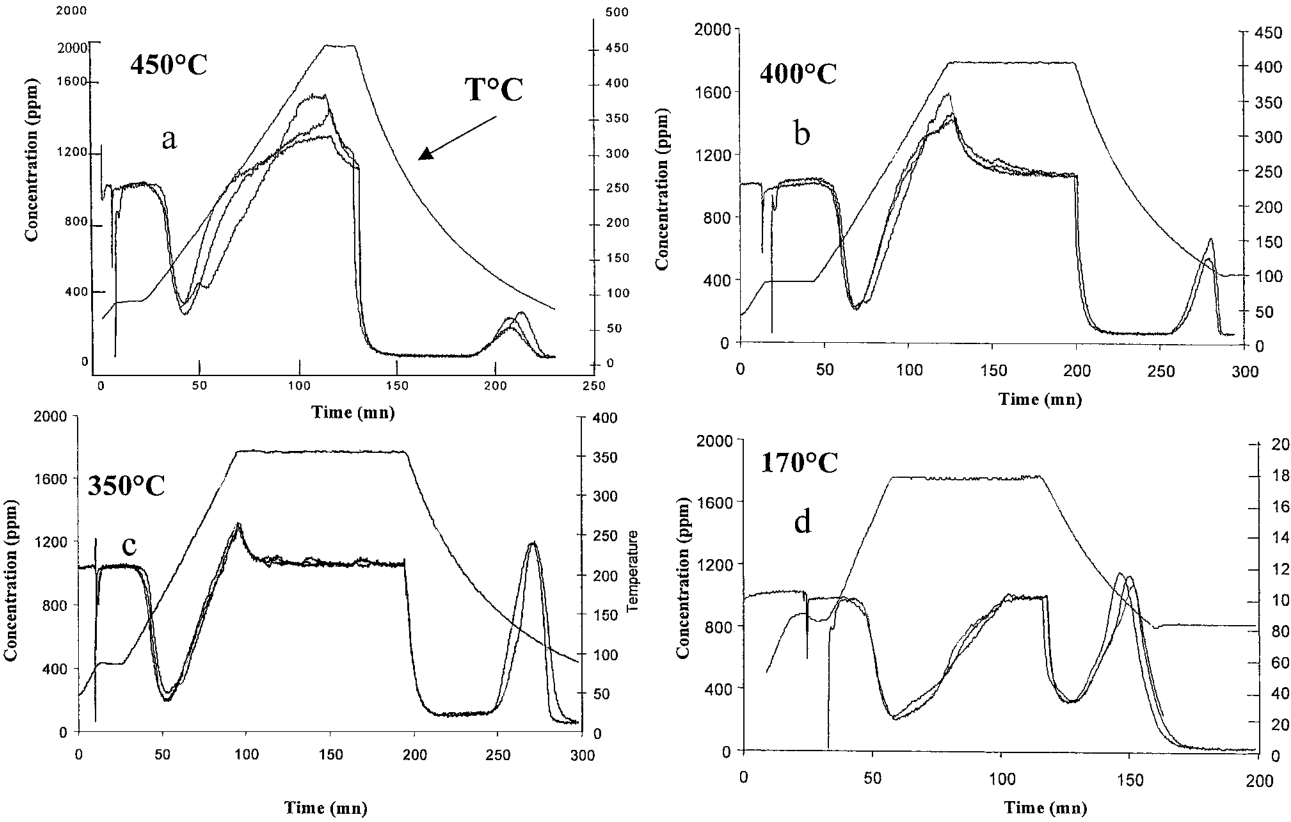

FIG. 3. Detailed profile of adsorption–desorption of NO and NO_2 adsorption in a lean-burn mixture; desorption in wet air with varying temperature of desorption: (a) 450°C; (b) 400°C; (c) 350°C; (d) 170°C.

The amount of NO_x trapped and released and the maximum temperature of operation are key parameters for practical application. The latter condition was further investigated by analysing the degeneracy of the structural properties following tests at different temperatures described above by XRD and FTIR.

The evolution of the structural properties with temperature as observed by XRD is reported in Fig. 4. The diagram

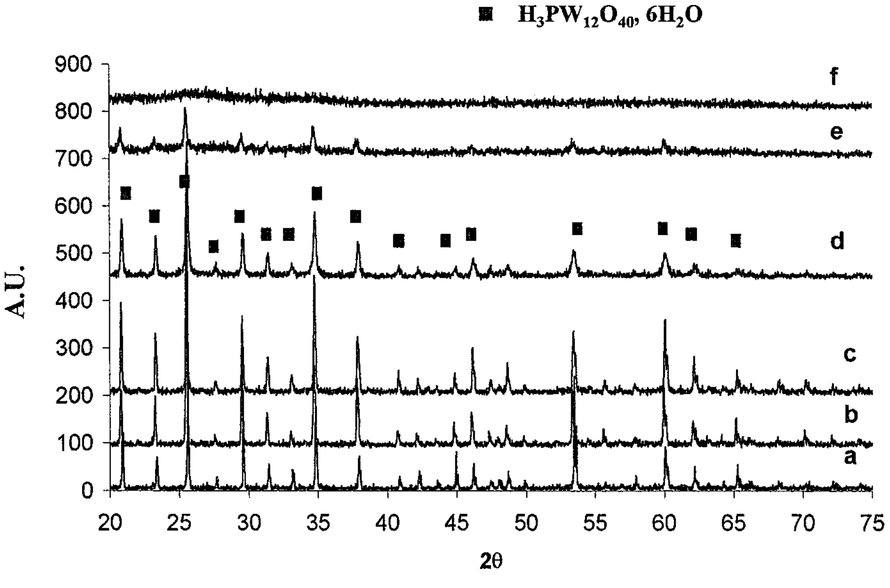

FIG. 4. XRD diagrams of $H_3PW_{12}O_{40} \cdot 6H_2O$ subjected to a lean-burn mixture (500 ppm NO, 500 ppm NO_2, 5% CO_2, 10% O_2, 5% H_2O: (a) 25°C; (b) 170°C; (c) 350°C; (d) 400°C; (e) 450°C; (f) 550°C.

of the solid at 25°C is in accordance with the literature (21). There is no evolution of the XRD structure when the HPW is exposed to a lean-burn mixture between 170 and 350°C. When the temperature reaches 400°C, the structure remains but a significant broadening of the XRD pattern lines is observed, accounting for a loss of crystallinity. Above this temperature, the degradation is such that the lines of diffraction are not observed anymore. This experiment was confirmed using FTIR, as illustrated by Fig. 5. Before exposure to a lean-burn mixture, bands at 596, 815, 890, 980, and 1080 cm^{-1} exist. The bands in the 600- to 1000-cm^{-1} region are characteristic of the Keggin structure. A complete resolution of the infrared spectrum is given by Rocchiocciolini-Deltcheff *et al.* (23). If the oxygen species are defined according to the nomenclature given by Misono (22), one can find four different species of oxygen, with Oi being an internal oxygen connecting P and W atoms, Oe, an edge-sharing oxygen connecting W's, Oc a corner-sharing oxygen connecting W_3O_{13} units, and Ot is the terminal oxygen bonding to one W atom. Then, the wavenumbers correspond to P–Oi for 596 and 1080 cm^{-1}, W–Oe–W for 815 cm^{-1}, W–Oc–W for 890 cm^{-1}, and finally W–Ot for 980 cm^{-1}. If the HPW sample is heated under a lean-burn mixture between 25 and 400°C, the IR spectrum remains strictly identical. Above this temperature, new bands around the existing one at 980 and 1080 cm^{-1} are formed. The formation of such bands corresponds to a distortion of the Keggin anion (24). New bands at 1057 and 1103 cm^{-1} indicate complete resolution of degeneracy with a lowering of the symmetry of the central PO_4 tetrahedron while the band at 964 cm^{-1} implies a degradation of the Keggin ion.

To summarise, following one experiment at 550°C, a complete loss of crystallinity was observed by both XRD and infrared in which profound modifications were notable in the spectrum. This degradation was accompanied by a loss of the capacity of absorption. The temperature limit at which this phenomenon is reversible for HPW is 400°C, which is within the range of temperatures feasible for practical application.

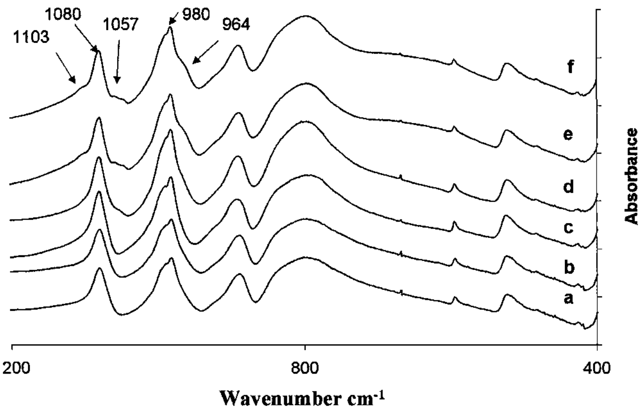

FIG. 5. IR spectra of $H_3PW_{12}O_{40} \cdot 6H_2O$ subjected to a lean-burn mixture (500 ppm NO, 500 ppm NO_2, 5% CO_2, 10% O_2, 5% H_2O: (a) 25°C; (b) 170°C; (c) 350°C; (d) 400°C; (e) 450°C; (f) 550°C.

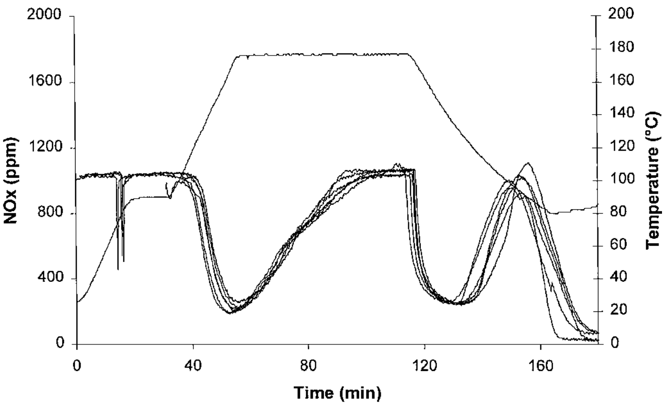

FIG. 6. Six successive runs of sorption/desorption on HPW of a lean-burn mixture: sorption 80–170°C; desorption by cooling under wet air (5% H_2O).

According to the experiments described above, absorption will be performed between 80 and 170°C and desorption will be carried out by cooling under wet air (5% H_2O). This set of experimental conditions was chosen because the maximum of absorption as described by Fig. 2 is at 170°C and at this temperature there is no thermal desorption. In Fig. 6 the data are presented for the six successive runs under these experimental conditions. These results reveal that the absorbent is perfectly stable, leading to the same amount of NO_x trapped over the six runs. The slight shift observed on the desorption peak arises from the difficulty in controlling the temperature ramp during cooling.

3.2. *Nature of the Absorbed Species*

To understand the nature of the interaction of the species absorbed on HPW in a lean-burn gas mixture, we have studied the effect of each gas present upon both absorption and desorption. The first experiment consisted of a detailed analysis of NO and NO_2 during these two phases under the experimental conditions defined above, i.e., absorption in a lean-burn mixture between 80 and 170°C and desorption while cooling in wet air (5% H_2O). The profile of such an experiment is shown in Fig. 7. In this case NO and NO_2 are sorbed in an equimolar ratio and their relative concentrations follow a similar evolution. The behaviour of these two components during the desorption phase was identical; i.e., they desorb at the same time in equimolar proportions. No absorption was observed in the case of an NO_2-free mixture, i.e., diesel conditions (Table 1); the explanation for this is the requirement of an HPW-type sorbent to undergo exclusively co-absorption of NO and NO_2. This ratio was varied between 0.2 and 5 and the same observations were noted; i.e., in all cases the quantity of NO adsorbed or desorbed is equal to that for NO_2. For this reason, no absorption was observed in the case of a NO_2-free mixture,

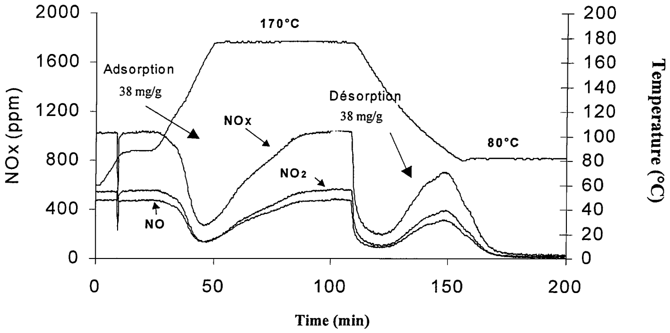

FIG. 7. Detailed profile of adsorption–desorption of NO and NO_2 adsorption in a lean-burn mixture with a maximum temperature of 170°C and desorption in wet air.

i.e., in diesel conditions. Nevertheless, the addition of 1% platinum promotes the oxidation of NO into NO_2 between 180 and 275°C. In this range of temperature, a consumption of 30 mg/g became possible using a diesel-type mixture. This necessity of undergoing co-absorption (i.e., no absorption was observed in the case of NO or NO_2 alone) contradicts the observation made by Bélanger *et al.* (20) who have previously shown that NO does not sorb in the absence of previously sorbed NO_2, as in our case, but NO sorbs with an increasing amount of presorbed NO_2 up to a maximum corresponding to equimolar quantities of NO and NO_2, thus implying that NO_2 can be sorbed on its own, in opposition to our observation.

3.2.1. Influence of various parameters upon absorption. To perform this study, experiments of sorption/desorption were carried out with a lean-burn mixture as described in Table 1 from which one gas is omitted, the flow being compensated with nitrogen. This comprises a series of three experiments described by Fig. 8: (a) without water; (b) without CO_2; (c) without O_2. Desorption always occurs in wet air (5% H_2O) by decreasing the temperature. It is observed that both CO_2 and O_2 have no influence on the absorption profile and the quantity of NO_x absorbed remains equal to 38 mg/g of HPW as obtained with a classical lean-burn mixture. Conversely, when absorption is performed in the absence of water, there is a significant shift of NO_x absorption toward lower temperature, the absorption starting at 80°C—this temperature being held 15 min before rampings; the NO_x concentration remained constant at 130 ppm during this entire stabilisation period and continued during the procedure of temperature ramping to be completed at 170°C. The absorption capacity, in the absence of water, remains equal to 38 mg/g of HPW. For the three experiments there were no noticeable changes in the desorption profiles; the slight shift observed is due to the difficulty in controlling the temperature when cooling.

In summary, this series of experiments revealed that there is no competition for absorption between CO_2 and NO_x, that oxygen is not implied in the absorption, and that water alone plays an influential role. This can be interpreted as a competition between H_2O and NO_x for the absorption sites, which is justified by a decrease in the temperature of absorption of NO and NO_2 in the absence of water.

3.2.2. Influence of various parameters upon desorption. To better understand the desorption process, the influence of each gas was studied separately. Up to now, humidified air (5% H_2O) has been used to perform desorption; to carry out this study, absorption is performed classically with a lean-burn mixture raised to 170°C and then desorption achieved by a modification of this mixture, the selective omission of one of the gases each time. The results of these experiments are displayed in Figs. 9 and 10. In each of these cases, the desorption mixture contained water, the question of the desorption without water being discussed in the next section.

Desorption under a nonmodified lean-burn mixture (Fig. 9) is possible but evolution is observed throughout the series of runs. Although the amount of NO_x trapped during the first run is similar to that observed previously, i.e., the amount of NO_x being 38 mg/g of HPW, the amount of NO_x

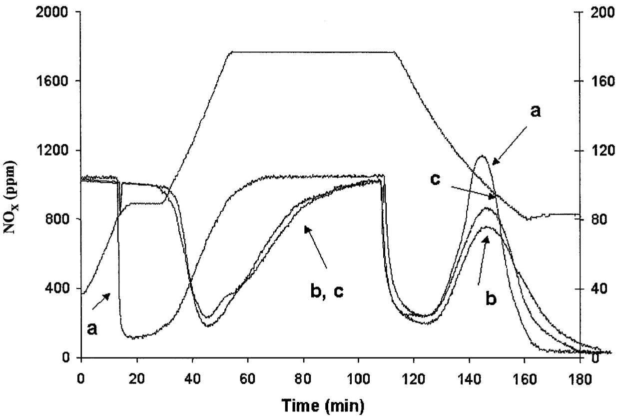

FIG. 8. Influence of each gas on NO_x sorption with a lean-burn mixture: (a) without H_2O; (b) without CO_2; (c) without O_2.

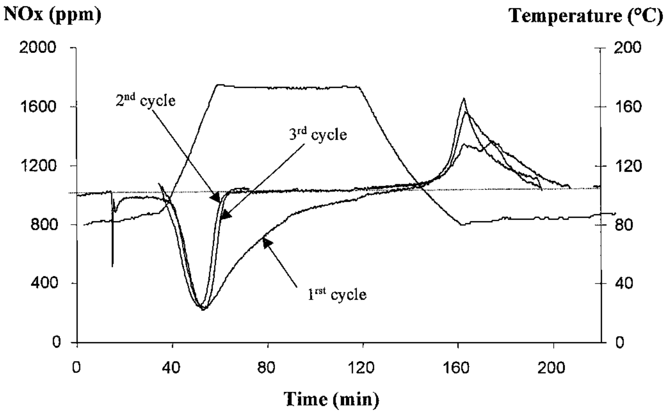

FIG. 9. NO_x absorption/desorption profile under a lean-burn mixture in both absorption and desorption.

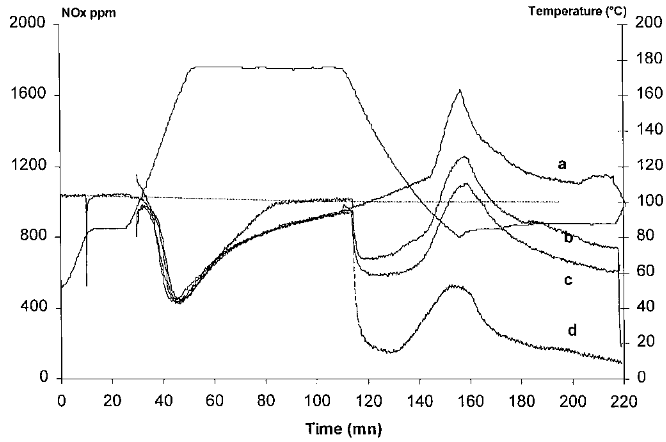

FIG. 10. Influence of each gas on NO_x desorption performed with a lean-burn mixture: (a) without CO_2; (b) without NO; (c) without NO_2; (d) without NO, NO_2, and O_2.

desorbed is only equal to 16 mg/g of HPW. This fact reflects the existence of equilibrium between the NO_x absorbed and the NO_x desorbed, which is due to the closed temperatures of each process. Indeed, absorption begins at ca. 100°C, just like the desorption. This incomplete desorption explains the decrease in absorption during the subsequent runs.

If NO or NO_2 is removed from the desorption mixture (Figs. 10b and 10c), the result is identical to that obtained with a desorption mixture containing only 5% H_2O in air, the amount of NO_x being the same and equal to 38 mg/g. Likewise, desorption is not affected by the absence of CO_2 or O_2 (Figs. 10a and 10d). Therefore, it can be concluded from this series of experiments that NO, NO_2, CO_2, or O_2 have no influence upon desorption.

3.2.3. Effect of water concentration. Water is an essential parameter to study since it is always present in an exhaust gas. In the absence of water from the desorption mixture and when cooling, desorption becomes impossible as presented in Fig. 11, the NO_x remains totally absorbed following the first run, the sites are unavailable for subsequent runs, and the profiles of both absorption and desorption are flat. These results illustrate the importance of water during both processes and confirm that there is a competition between H_2O and NO_x for the absorption sites as demonstrated earlier by a decrease in the temperature of absorption of both NO and NO_2 in the absence of water. To ratify the essential role of water, a detailed study of the influence of water concentration upon desorption was undertaken and is reported in Fig. 12. The concentration of water was varied between 0 and 10%.

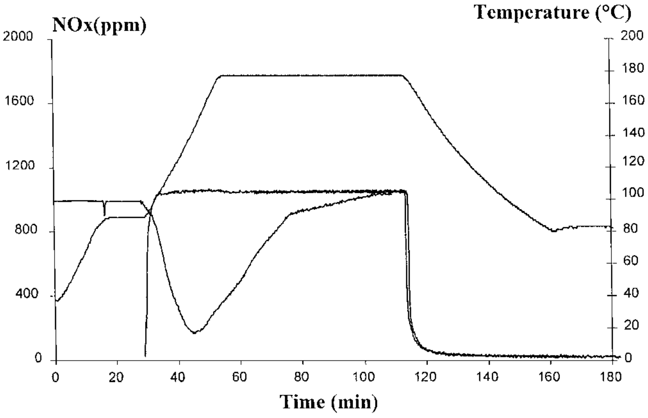

FIG. 11. NO_x absorption: three runs of absorption of a lean-burn mixture and desorption in air without water.

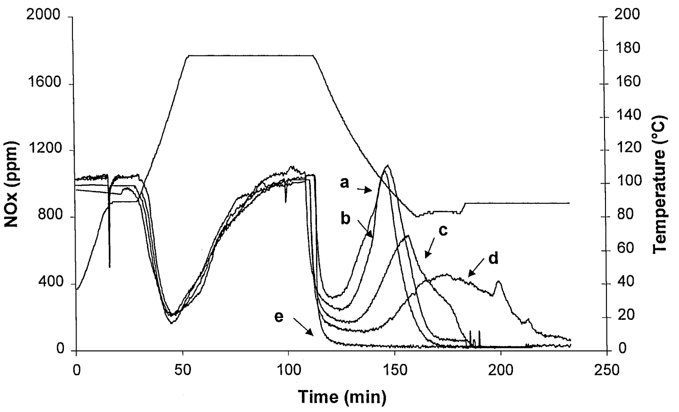

FIG. 12. Influence of water concentration upon desorption: (a) 10%; (b) 5%; (c) 1.4%; (d) 1%; (e) 0%.

For 5 and 10% water in the desorption phase, this decrease of H_2O concentration did not affect either the amount of NO_x desorbed or the profile of desorption. Nevertheless, when the percentage of water was reduced, the desorption peak broadened, yet the amount of NO_x desorbed remained unchanged, even with only 1% water. Without water, no desorption was observed.

3.3. Mechanistic Studies

3.3.1. Infrared. HPW was saturated with NO and NO_2 at 170°C and then examined by infrared. The HPW is diluted in KBr and the spectrum recorded at 25°C is presented in Fig. 13b and compared with a fresh sample displayed in Fig. 13a. On the reference HPW a broad band with two maxima at 1620 and 1710 cm^{-1}, have been identified as corresponding to water and $H^+(H_2O)$ bridges in the secondary unit, respectively. Upon submission to NO_x new bands at 1295, 1384, and 2261 cm^{-1} appear. According to Bélanger and Moffat (25), the band at 2261 cm^{-1} can be attributed to a disturbed NO_2^+ species and more particularly to HNO_2^+. In the case of NO adsorption on HPW presaturated with NO_2, observation of the appearance of a new band at 1304 cm^{-1} was attributed to the N_2O_3 species. Nujol, used in the recording of infrared spectra, has bands between 1350 and 1450 cm^{-1}, which may possibly hide the band at 1384 cm^{-1}. According to Chen and Yang, the band

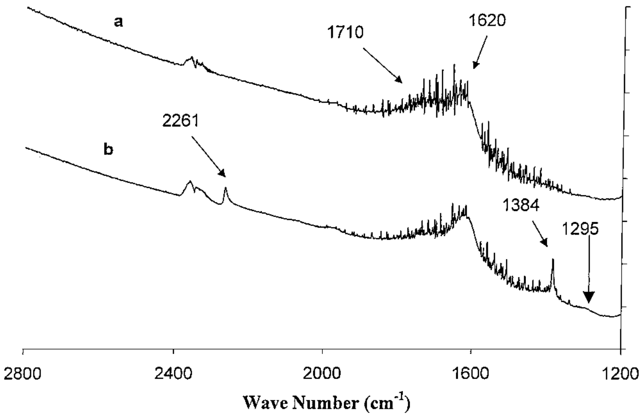

FIG. 13. IR spectra of HPW: (a) fresh; (b) saturated with NO_x.

at 2261 cm^{-1} is due to the presence of an NO^+ species and more particularly to $(N–O–H)^+$. The same authors suggest that the bands at 1384 and 1295 cm^{-1} are due to the interaction of NO with the KBr used to press the HPW sample (26). Our interpretation is somehow very different. Since NO and NO_2 are adsorbed simultaneously and in equal proportions and with our consideration of the literature (27, 28), we attribute the band at 2261 cm^{-1} to an NO^+ species interacting with the proton of the structure. The modification of the electronic environment of NO^+ could explain the shift in energy when compared to free NO^+, which is normally observed at 2330 cm^{-1} (29). IR vibrations for nitro and nitrito species are reported in the 1200- to 1400-cm^{-1} region (27). We attribute the bands observed at 1295 and 1384 cm^{-1} to a $(^-O–N{=}O)$ species stabilised in the acid structure by interaction with both the proton and the terminal oxygens of the Keggin units.

3.3.2. Equilibrium NO_x/H_2O. As confirmed by the experiment in Fig. 12, water plays an influential role with respect to the properties of HPW. Therefore, further investigation was performed, an experiment specific for the purpose as described in Fig. 14. Following standard NO_x absorption, the temperature was reduced to 80°C, confirming the absence of NO_x desorption (150 to 180 min of the *x* axis); then a mixture of 5% water in air was introduced (minutes of 180) and immediate desorption of NO and NO_2 was obtained, an amount of 38 mg corresponding to the quantity previously absorbed. Once the desorption was completed (250 min), the water supply was interrupted and an NO_x absorption experiment was carried out. In this case, the absorption started at 80°C instead of 100°C, as observed previously in the presence of water; the amount of NO_x trapped remained the same.

This experiment yielded strong evidence for the importance of water: while absorption is possible in the absence of water, desorption is inhibited but this inhibition is reversible since, upon subsequent water addition in the gas stream, complete desorption is obtained. These operations of absorption and desorption in the absence of water are non destructive since the absorption capacity remained unchanged. The absorption of H_2O and NO_x is competitive and is the result of equilibrium between these species. This equilibrium exists between 80 and 100°C and shifts with the temperature as follows:

—Below 80°C, the absorption of water is favoured.

—Above 100°C, equilibrium is displaced toward a preferential absorption of NO and NO_2.

The stability of water in the HPW structure was then studied by TGA as described by the profile of mass loss versus temperature in Fig. 15. The overall mass loss is equal to 12.4% distributed across three temperature zones. The first is between 25 and 75°C and is equivalent to 80% of the overall mass loss. This important quantity is due to the

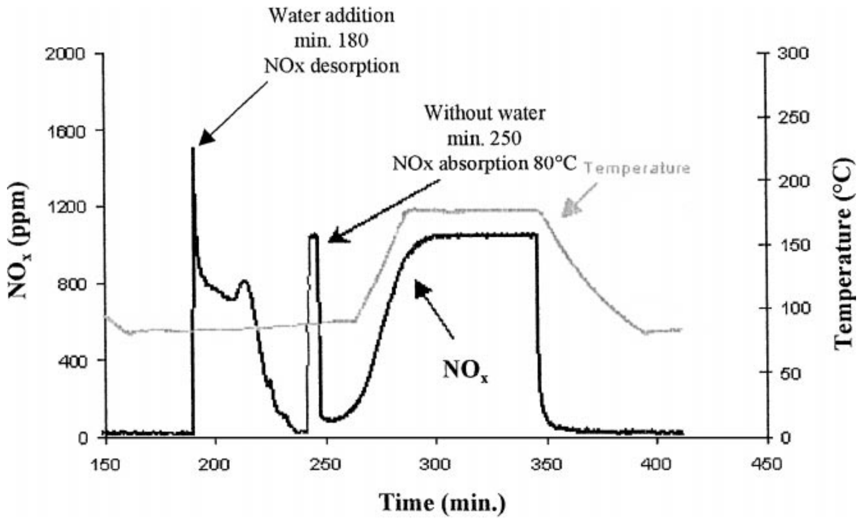

FIG. 14. Effect of transient addition or removal of water on the desorption (180-min addition) and the absorption (250-min removal) of NO_x.

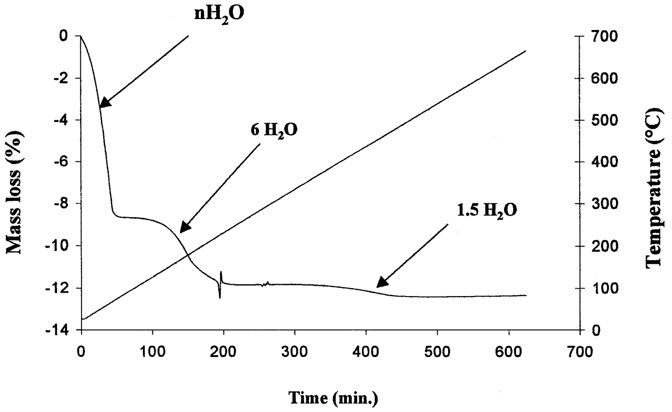

FIG. 15. Thermogravimetric analysis of HPW (temperature ramp of 1°C/min).

presence of physisorbed water and varies according to the temperature of the pretreatment. For example, following calcination at 300°C, this zone of water production disappeared. The second zone between 100 and 240°C represents 3.2% and its integration showed that it corresponds to the structural water molecules. The final loss occurred between 400 and 475°C and resulted from the decomposition of $H_3PW_{12}O_{40}$ to simple oxides, giving 1.5 water molecules as

$$H_3PW_{12}O_{40} \rightarrow \left(\tfrac{1}{2}\right)P_2O_5 + 12WO_3 + \left(\tfrac{3}{2}\right)H_2O.$$

The most interesting mass loss is that occurring between 100 and 240°C since its temperature corresponds to that of NO_x absorption (100–300°C). There is a correlation between the departure of water and NO_x absorption. Conversely, during the desorption step NO and NO_2 are replaced by water. Complementary experiments displayed in Fig. 16 confirm that the water evacuated in this temperature zone is of the most importance. In this experiment, the HPW was first heated to 300°C to remove both physisorbed and crystallised water, then cooled to 200°C (phase 1), and finally brought into contact with NO and NO_2 in the absence of water (phase 2). During this phase, NO_x is not absorbed. The HPW is subsequently cooled to 80°C under wet air (phase 3) and a classical lean-burn test is performed (absorption: lean-burn mixture containing 5% water; desorption: 5% water in air) (phase 4). During this latter phase, the absorbent performed as expected, i.e., 38 mg/g of NO_x were trapped and then desorbed upon cooling. From this experiment, we can conclude two important points:

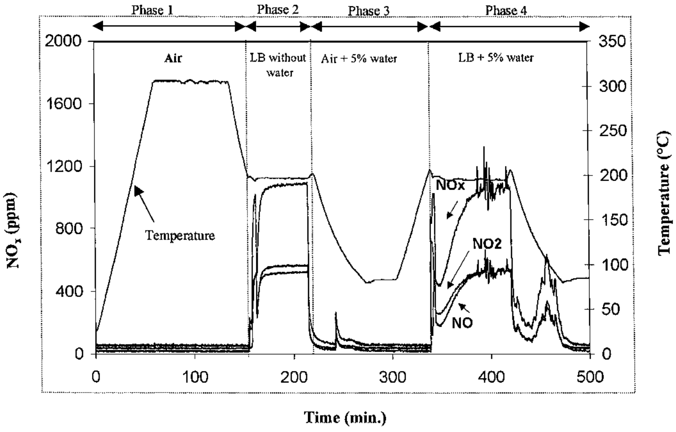

FIG. 16. Absorption of NO_x on HPW after removal of structural water (phases 1 and 2) and recovering of water molecules (phases 3 and 4).

—The water that is replaced by NO and NO_2 is provided by the crystallisation water molecules.

—The presence of the secondary structure, i.e., the $(H_2O)_2H^+$ bridges, is necessary to obtain an NO, NO_2 exchange.

Finally, the role of acidity was investigated by substituting the three protons of the structure by Na^+ using an Na_2CO_3 solution at room temperature to form the corresponding structure $Na_3PW_{12}O_{40}$. In this case, the absorption capacity diminished, confirming the importance of Brönsted acidity in the absorption process. Bélanger and Moffat showed earlier that the acidity of the heteropolyacids is a major factor in its sorption properties for NO_2 (20).

3.3.3. Mechanism. The mechanism of NO_x adsorption has already been discussed in the literature with the propositions of the teams being somewhat different. For Chen and Yang (26, 30), NO only interacts with HPW to substitute for water molecules at temperatures between 50 and 230°C and low NO concentrations. Upon rapid heating, NO is reduced to N_2. The mechanism invokes the formation of N_2 via an $(NOH)^+$ complex, replacing the $H^+(H_2O)_2$ linkages in the structure. This suggestion is based upon NO thermodesorption, XRD results, and bond length calculations. In their case, however, Bélanger and Moffat (20, 31) have observed that NO_2 is adsorbed with a stoichiometry of 3 molecules of NO_2/Keggin anion, which resulted from the reaction between NO_2 and surface or bulk protons. The exposure of the solid to water vapour at 150°C led to a partial desorption of NO_2 into HNO_3. In the same paper, they also suggested that NO_2 can be reversibly removed by exposure to water vapour at 150°C. NO is not able to penetrate the bulk of the structure and is therefore not adsorbed onto the structure. Nevertheless, if NO_2 is preadsorbed, some NO adsorption is observed and such a phenomenon is related to the formation of N_2O_3, as suggested by infrared spectroscopy results. In a later paper by Herring and McCormick, it is suggested that NO displaces water to give an $NOH^+ \cdot H_2O$ intermediate, which causes rearrangement of the hydrogen bond secondary structure (32). This explanation presents many similarities to the previous one.

Based upon our experiments, our interpretation is quite different: There are two key factors for the NO_x

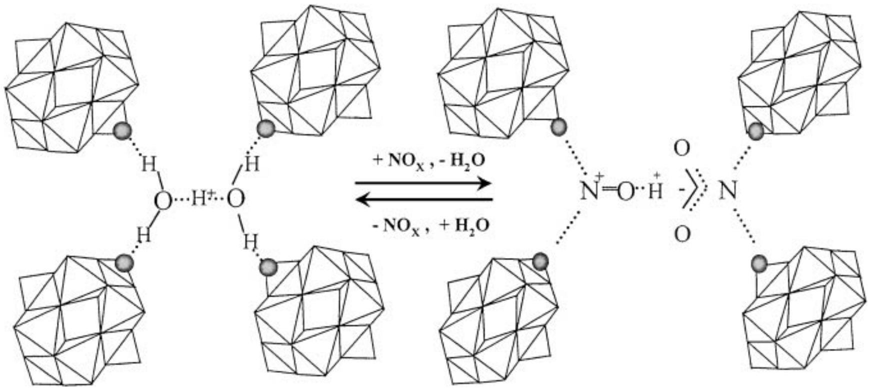

FIG. 17. Mechanism of NO_x absorption–desorption on HPW.

adsorption/desorption process; the first one is the co-absorption and the co-desorption of NO and NO_2, while the second one is the presence of water. The absence of water during the adsorption phase leads to a reduction in temperature of ca. 20°C. This is indicative of a competition between NO/NO_2 and water for the adsorption sites. In the absence of water from the phase of desorption, no desorption is observed at all. However, as soon as water is added to the mixture, desorption of NO_x becomes immediately possible. These successive operations of adsorption–desorption with/without water are perfectly reversible and nondestructive since the initial capacity of 38 mg/g is always recovered.

These observations have led us to propose a mechanism of adsorption and desorption of NO_x on HPW. The adsorption proceeds via a substitution of the water molecules by NO_x to form an $[H^+(NO_2^-, NO^+)]$ complex, as presented in Fig. 17. This process is a bulk phenomenon and is not related to the surface since the amount of NO_x adsorbed corresponds to complete substitution of water; i.e., stoichiometrically, 6 molecules of water are replaced by $3(NO^+, NO_2^-)$. Moreover, the temperature at which adsorption occurs correlates perfectly with the TGA experiment (Fig. 15), which reveals that structural water is evolved between 100 and 300°C. Once substitution is achieved, the cohesion of the secondary unit is maintained by this complex $[H^+(NO_2^-, NO^+)]$. Complementary evidence from XRD suggests that the HPW structure is observed following complete saturation by NO_x save for a shift of the lines toward higher 2θ. The presence of H^+ in the structure is essential to the mechanism since the complete substitution by Na^+ led to a solid with no NO_x absorption capacity.

CONCLUSIONS

The aim of this work was to the study the NO_x absorption/desorption process upon HPW, a solid from the heteropolyacids family. This catalyst presents the following outstanding characteristics:

—Absorption capacity is both very high and results from co-absorption of NO and NO_2 in an equimolar ratio.

—The existence of two types of desorption mode: the first by heating, which led to a progressive degradation of the HPW due to a loss of crystallinity, the maximum temperature being 450°C; above this temperature, the structure is irreversibly destroyed. The second type of desorption is obtained by cooling under wet air, this method being completely reversible and reproducible. The temperature of desorption is lower than the temperature of absorption, a remarkable observation.

—High stability with respect to time was obtained (>50 h); no deactivation with time was observed when the catalyst was used at 170°C. At this temperature, it is possible to get 50% conversion of NO into NO_2 in the presence of platinum, rendering therefore the HPW impregnated by 1% Pt active for the absorption of NO_x, resulting from both a diesel and a lean-burn engine.

The detailed studies of the various parameters influencing the overall process revealed the major role of water and the specificity of the absorption site for NO and NO_2 and therefore the absence of competition from other molecules present in a lean exhaust gas (such as unburned hydrocarbons or CO_2). The different steps of the adsorption–desorption process on HPW can be summarised in the following manner:

In the first step, physisorbed water is evacuated between 25 and 80°C. Then, as a result of the *in situ* polarised character of the HPW molecule, between the proton and the oxygen, i.e., the presence of an electrostatic field, a single-electron transfer is initiated according to $NO + NO_2 \rightarrow NO^+ + NO_2^-$. Infrared spectroscopy indicated the existence of these species. Once the temperature reaches 100–120°C, the simultaneous adsorption of NO and NO_2 occurs by the substitution of structural water molecules with the formation of a $[H^+(NO_2^-, NO^+)]$ complex. During the cooling phase and in the presence of water, around 100°C, reverse substitution occurs. The presence of the proton in the initial structure is likely to be essential since its substitution by Na^+ led to a solid with no absorption properties.

The cooling process is probably one of the most remarkable features of this adsorbent. Similarly, the use of such a technique will surmount the problem of thermal fragility in heteropolyacids while opening up new possibilities of research toward practical applications for elimination of NO_x arising from diesel engines.

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