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NO_x sorption–desorption study: application to diesel and lean-burn exhaust gas (selective NO_x recirculation technique)

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Abstract

NO_x adsorption/desorption capacities of barium aluminates and $BaSnO_3$ were measured under representative exhaust gas mixture at temperatures below 550°C and compared to those of bulk BaO. The capacities are high and the test of sorption–desorption is reproducible on barium aluminate and $BaSnO_3$, while this is not the case on BaO. The difference is due to the electronic environment of barium oxide. If BaO is not engaged in a chemical bond, progressive formation of high stability carbonates is observed. This is not the case with barium aluminate and $BaSnO_3$, where carbonation does not take place because the competition between nitrate and carbonate formation is in favour of the nitrate due to its chemical nature. An N-bounded nitrate, with IR frequencies at 1360 and 1415 cm^{-1}, is formed on barium aluminate and $BaSnO_3$ and not on bulk BaO. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Lean-burn exhaust gas; Diesel; Selective NO_x recirculation

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1. Introduction

The atmospheric pollution by NO_x is originated mainly from the transportation sector, which accounts for almost 70% of it. To reduce the emission of this pollutant from an exhaust gas has become a dominant challenge in the field of diesel or lean-burn engines technology. In the recent years, two main approaches have been developed: in the first one, the NO_x are reduced on stream and continuously either by the unburned hydrocarbons emitted by the engines or through the addition of hydrocarbons or urea into the exhaust stream — this latter possibility being considered more for trucks and buses [1,2]. This is the so-called selective catalytic reduction of NO_x (SCR). Although many catalytic systems have been developed in the past few years, there are major drawbacks. For example, most of the systems contain precious metals which only operate in a narrow range of temperature and often produce significant amounts of N_2O, not yet regulated but with well-known greenhouse effect and also affecting the ozone cycle in the stratospheric atmosphere. The second approach is designated as a NO_x storage and reduction catalyst (NSR) and was developed for lean-burn engine, the catalyst usually contains a NO_x sorbent composed by a phase of BaO dispersed over alumina. In this case NO_2 is stored on BaO and a subsequent reduction proceeds by action of a noble metal generally Pt or Rh [3–5] and by lowering the oxygen concentration to stoichiometric or even rich conditions. Here again, although higher NO_x conversion as compared with SCR is obtained, some major inconvenients remain, essentially due to the severe poisoning by sulphur when operating rich with lean-burn engines, leading to the need to develop a

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regeneration procedure and to the impossibility to operate rich with diesel engine. To face the problem linked to SCR and NSR technologies, Daimler–Chrysler have developed a very attractive technique called SNR (selective NO_x recirculation), whereby NO_x gases are recirculated to the combustion chamber, where they are reduced by combustion processes following selective sorption [6]. The main advantages of this technique are due to the fact that no by-products or secondary emissions will be produced and that the system works without the need to manage the engine operation.

The key point in technologies where NO_x sorption is involved (i.e. NSR or SNR) 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 these resultant gases at temperatures a little higher (maximum 550°C). These systems are numerous and are mainly based upon inorganic oxides [7], mixed oxides [8,9], well-defined structures such as perovskites [10], cuprates [11] or modified three-way catalysts [12]. The most efficient of these formulations contain barium oxide, which easily convert to nitrates [13], but they absorb selectively NO_2 and not NO [14]. To our knowledge, for the sorption of NO_x, the oxides containing an alkali or an earth alkali element are the most active of those reported in the literature [15]. Because of its basicity, barium oxide is very likely to form nitrates and this sorbent fulfils several of the necessary requirements, among them is the necessity to form and decompose nitrates in a suitable range of temperature for diesel application (100–500°C). Therefore, we have decided to focus our attention on structures containing barium within a variety of electronic environments in a well-crystallised structure. From amongst them, we have developed a new type of material from the family of barium aluminates ($BaAl_2O_4$, $BaAl_{12}O_{19}$), and in keeping with this idea, we have also elected to use perovskites ($A^{2+}B^{4+}O_3$). Preliminary results obtained in the laboratory have revealed that among perovskite structures, $BaSnO_3$ was the most interesting towards NO_x sorption [14]. All these materials were tested for their NO_x storage and release ability and compared with barium oxide in conditions as close as possible to those of a real diesel or lean-burn engine.

The work was carried out within the framework of the SNR Brite–Euram European project. The project partners were Daimler–Chrysler, AG and Johnson Matthey as industrial partners and the Universities of Leuven (COK) and Gothenburg (Chalmers). One of the main objectives consists of the development of a material which is able to selectively trap NO_x released from both lean-burn or diesel engines.

2. Experimental

2.1. Preparation of the catalytic material

Barium aluminates have been developed as high temperature materials for methane combustion especially by the team of Machida et al. [16] and Groppi et al. [17]. The method of preparation is the one described by Groppi et al. which is easy to implement and yields reproducible characteristics. Succinctly, the required amount of $Ba(NO_3)_2$ was dissolved in distilled water and the solution acidified to pH=1 with dilute HNO_3. A solution of $Al(NO_3)_3{\cdot}9H_2O$ was then added. This combination was poured into an $(NH_4)_2CO_3$ solution and this new mixture heated at 60°C for 3 h before being filtered. All solutions were stirred throughout. The solid was washed to remove remaining nitrates and dried overnight in an oven at 120°C. Finally, the powder was calcined in an air flow at 1000°C. With this temperature, it is not possible to get a pure phase of barium aluminate, but only a mixture of $BaAl_2O_4$ and Al_2O_3 with traces of the hexa-aluminate ($BaAl_{12}O_{19}$) phases were identified by XRD. The BET surface is equal to $90\,m^2\,g^{-1}$.

Perovskites are mixed oxides with the general formula ABO_3, where the element A is generally a rare-earth or an earth-alkali metal, while element B is a transition element (3d, 4d or 5d) [18]. In this structure, the cation B occupies an octahedral site surrounded by six oxygens. Cation A, which is more voluminous, is surrounded by 12 oxygens and occupies a dodecahedral site [19]. Following the formula, $BaSnO_3$, the perovskite was prepared by the sol–gel like method. The preparation of $BaSnO_3$ (1 g) proceeds by the solubilisation in propionic acid (50 ml) of barium acetate (0.84 g) and metallic tin (0.39 g) until a limpid solution is obtained. The two solutions are then mixed together and stirred for 30 min before the final stage, which is the evaporation of the propionic acid and subsequent calcination of the translucent residue at 750°C for 4 h at 4°C min^{-1}. The characteristic lines of the perovskite spectrum were obtained by XRD with this temperature of calcination, but the presence of well-crystallised $BaCO_3$ and SnO_2 in weak proportion was also identified. The resulting BET surface was 14 $\mathrm{m}^2\,\mathrm{g}^{-1}$.

2.2. Experimental set-up

The experimental set-up was designed in the laboratory. The experiments were conducted in a flow reactor using a series of mass flow controllers with diluted gases (NO, NO_2, CO, C_3H_6, O_2, CO_2, SO_2, with N_2 as the diluting gas). The reactor was a quartz tube of 12 mm in diameter and a sinter sealed up with Cajon couplings. The uptake and desorption capacity of NO/NO_2 were measured in the range 80–550°C, using a furnace and a temperature controller with a mass of catalyst of 330 mg and a flow of 300 $\mathrm{cm}^3\,\mathrm{min}^{-1}$. The exact temperature was measured by a thermocouple in contact with the catalytic bed. Water was added using a saturator maintained at the required temperature in order to have 5% humidity in the flow. The water was removed from the stream with a permutation tube and the NO and NO_2 were specifically examined by infrared analysers (Rosemount, accuracy ±10 ppm), but the other gases were not. Punctual examination of N_2O was performed. Nevertheless, this product was not identified in the flow. Computer with a special software written in the laboratory drove the apparatus. The amount of NO_x trapped and then released upon desorption was estimated by integration of the curve below or above the baseline (1000 ppm) for sorption or desorption, respectively, and is expressed as mg of NO_x per gram of catalyst. Since both signals of NO and NO_2 are recorded, this value is exact.

2.3. Gas composition

For this study, a lean-burn gas was chosen to model sorption. Generally, a lean-burn mixture contains both NO and NO_2, while a diesel mixture contains only NO. The reason of this choice lies in the fact that on a real exhaust system in the case of a diesel engine, an oxidation catalyst is placed before the sorbent bed in order to transform, at least partially, NO into NO_2 and to oxidise the unburned hydrocarbon. In such way, the sorption of NO_x is easier and a possible poisoning by carbonaceous deposit is avoided. The mixture used for this study consists of 500 ppm NO, 500 ppm NO_2, 5% CO_2, 10% O_2 and 5% H_2O, the eluant being nitrogen.

2.4. TGA/MS

In certain cases, thermogravimetric and thermodifferential analyses were undertaken in order to check the nature of the gases either sorbed or desorbed. 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 catalyst was tested following an experiment when it was submitted to the lean-burn gas composition with no desorption phase. The crucible containing about 100 mg of catalyst was heated up to 980°C in air with a ramp rate of 10°C min^{-1}, while both heat transitions and mass loss were recorded. Masses 12 (C), 18 (H_2O), 28 (N_2 or CO), 30 (NO), 44 (CO_2) and 46 (NO_2) were followed by mass spectrometry. It should be noted that NO_2 was almost undetectable by mass spectrometry, and that the parent peak which represents ca. 95% of the signal appeared at $m/e=30$.

2.5. IR studies

A fraction of the catalyst was pressed in the form of a KBr pellet. The same masses of KBr (100 mg) and sample (3 mg) were used for all the solids and the IR spectra reported result from a previous subtraction of the blank. The IR spectra were recorded using a Nicolet 5DXC through a spectral domain between 400 and 4000 cm^{-1} with a 2 cm^{-1} resolution, which included the prior subtraction of the blank.

3. Results and discussion

3.1. Sorption/desorption profiles

The sorption profiles for the three samples prove to be very different, as represented in Fig. 1. Principally, when submitted to a mixture of gas representative of a lean-burn exhaust, the barium aluminate undergoes sorption of NO_x ($20\,\mathrm{mg{\cdot}g}^{-1}_{\mathrm{catalyst}}$) in the range of

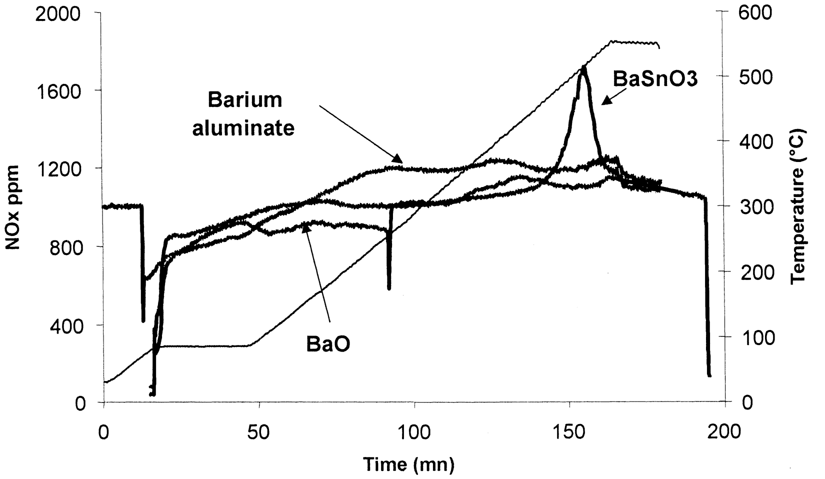


Fig. 1. NO_x sorption/desorption profile with a lean-burn mixture on bulk BaO, first run, barium aluminate and $BaSnO_3$.

temperature between 80 and 330°C, and then a complete desorption of NO_x is observed from 330 to 550°C. The value of the amount of NO_x trapped and desorbed over the number of runs is reported in Table 1. While this process remains perfectly reproducible, it should be equally noted that deactivation was not at all evident. In the case of $BaSnO_3$, the sorption of NO_x occurs mainly during the 30 min isotherm at 80°C, and continues when the temperature is raised to 350°C. The desorption is observed above 380°C and contrary to barium aluminate, occurs with a sharp profile. Again, the amount of NO_x trapped is always equal to the amount of NO_x desorbed upon heating. Furthermore, the phenomenon of sorption/desorption is perfectly reproducible and can be repeated many times without deactivation. The value of the amount of NO_x trapped and desorbed over the number of runs is given in Table 1.

Table 1
Amount of NO_x trapped and desorbed over three runs using a lean-burn mixture

	Amount of NO_x (trapped/desorbed) ($mg{\cdot}g_{catalyst}^{-1}$)		
	Run 1	Run 2	Run 3
BaO	15/8	2/4	2/2
Barium aluminate	20/20	20/20	20/20
$BaSnO_3$	16/16	16/16	16/16

For BaO however, the behaviour proved to be different. Bulk BaO led to a sorption of NO_x ($15\,mg{\cdot}g_{catalyst}^{-1}$) between 80 and 280°C, but only to a small desorption which began at 550°C, the maximum temperature used in the standard test. The sorption capacity was measured only during the first test. Contrary to the other catalysts studied in this work, it was not possible to obtain reproducible quantities of sorbed NO_x during successive runs with BaO, but instead, a decrease of the sorption capacity was observed when comparing the first three runs, from ca. 15 to 2 mg of NO_x per gram of catalyst (Table 1). Nevertheless, an increase of temperature to 650°C led to complete desorption of the NO_x previously sorbed.

3.2. Nature of the species formed during the sorption process

Following the examination of trapping ability, the composition of the gas sorbed (NO or/and NO_2) was investigated for all the samples. An example is presented in Fig. 2, where variations of NO, NO_2 and NO_x were studied during a single experiment on $BaSnO_3$ as a function of temperature and time. This graph reveals that only NO_2 is absorbed between 80 and 350°C and that NO is never trapped. A significant increase in the NO concentration from 500 to 600 ppm at 80°C is also observed at the beginning of the absorption phase. The

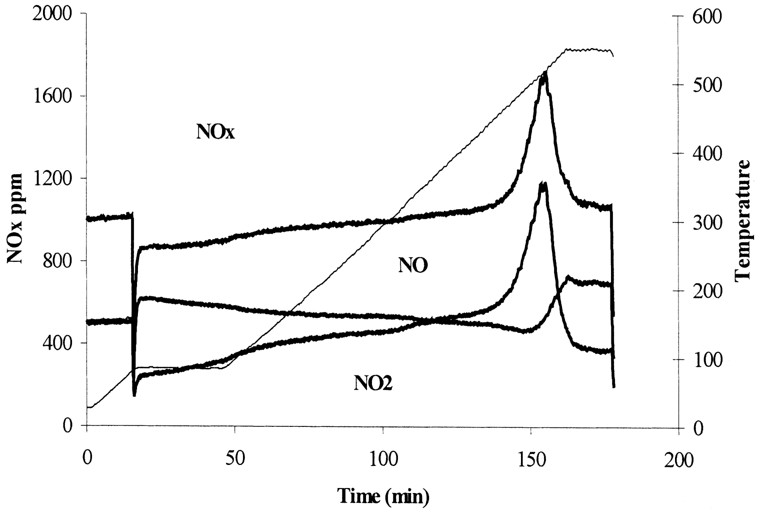


Fig. 2. Detailed NO and NO_2 sorption/desorption profile with a lean-burn mixture $BaSnO_3$.

NO concentration comes back to its initial value when the temperature of 350°C is reached.

The desorption starts at 420°C and finishes at 550°C. During this phase only NO_2 is found in the gas phase. Furthermore, from 450°C, an increase of the NO concentration above its initial value is observed. This is a thermodynamic relation between NO and NO_2 whereby, in the presence of oxygen, NO is favoured at high temperature [20].

An example of the sorption/desorption profile with detailed NO, NO_2 analysis on barium aluminate is given in Fig. 3. Here again, only NO_2, and not NO, is trapped between 80 and 200°C, but a point of difference with $BaSnO_3$ is the profile of desorption as mentioned above. NO_2 constantly desorbs in a broad range of temperature 200–550°C exhibiting three peaks with maxima at 280, 400 and 550°C. Because of the large variety of barium aluminates, one can think that these

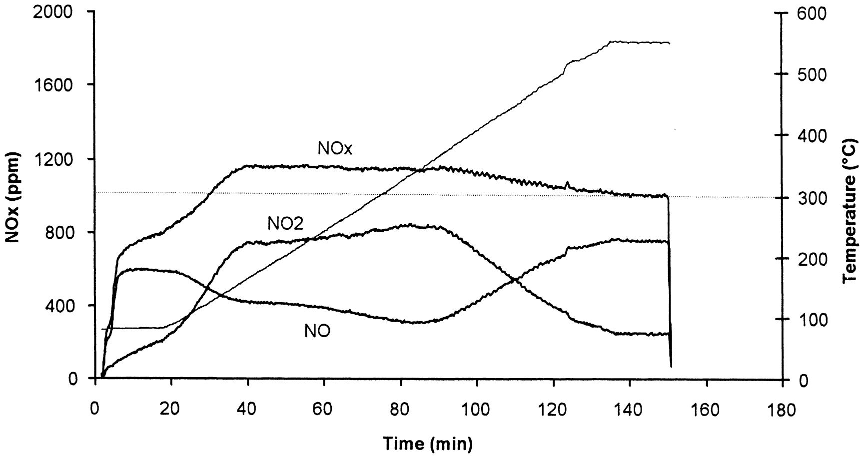


Fig. 3. Detailed NO and NO_2 sorption/desorption profile with a lean-burn mixture barium aluminate calcined at 100°C.

three peaks correspond to the decomposition of nitrates formed on barium oxides with different electronic environment.

The various species were then identified by FT-IR. In order to ease the detection of the infrared bands, a fraction of the solid examined by FT-IR was withdrawn from the reactor where the sorbent had been submitted to the lean-burn mixture three times following the standard procedure. Since in this procedure, the catalyst is heated at 550°C, all the nitrate species are decomposed at this temperature to barium aluminate and $BaSnO_3$. This is witnessed by the fact that the baseline comes back to the original NO_x concentration (i.e. 1000 ppm) when this temperature is reached. Therefore only carbonates could be identified using this procedure.

To observe the formation of nitrates, the sample was exposed to the lean-burn mixture at 25°C for 2 h in the case of bulk BaO and barium aluminates, and 3 h to the same mixture at 80°C in the case of $BaSnO_3$.

In Fig. 4, the formation of carbonates during three successive lean-burn experiments is shown for (a) BaO (b) barium aluminate and (c) $BaSnO_3$. In each case, the comparison of the spectrum for a fresh sample (calcined at 630°C in the case of BaO to remove humidity and atmospheric carbonates) with the reacted one is given. The infrared spectrum of bulk BaO before any treatment presents bands at 850, 1060, 1430 and 1750 cm^{-1}.

The infrared spectrum of untreated BaO subjected three times to a mixture of NO, NO_2, CO_2, H_2O and O_2 between room temperature and 550°C and cooled down in air to 25°C comprises the same bands as the one on BaO calcined at 630°C, but their respective intensities are increased considerably. According to Li et al. [21] and Nakamoto [22], the bands at 850, 1060, and 1430 cm^{-1} are assigned to a unidentate carbonate. Normally they should be accompanied by a band at 1395 cm^{-1}, but this proves difficult to see excepting as a weak shoulder in the broad band at 1430 cm^{-1}. The assignment of the band at 1750 cm^{-1} might correspond to bridged carbonates, but it is more probable that it is related to an asymmetric bending CO_2 resulting from the adsorption of CO_2 upon metallic oxides at low temperatures [23,24].

Our experiments indicate that unidentate carbonates exist upon the barium oxide before any pre-treatment. They appear to be very stable since they resist decomposition even under thermal treatment in temperatures as high as 630°C. Exposure to CO_2 contained in the gas phase only led to an increase of their concentration revealing a carbonation of BaO during the lean-burn tests.

On barium aluminate, the spectra of carbonates before and following reaction between 80 and 550°C are much simpler. In fact, they are the same with very poorly resolved bands of weak intensities present at 1440 and 1395 cm^{-1} representing a small amount of surface, unidentate carbonates. Due to the structural band of aluminates, frequencies below wave number of 1000 cm^{-1} cannot be read. The main point to note is that in contrast to carbonates formed upon BaO, there is no formation of new carbonates on barium aluminates after several lean-burn tests.

The IR spectrum of $BaSnO_3$ resembles more to the one of bulk BaO with bands at 850, 1060, 1430 and 1750 cm^{-1}. According to the literature, the bands at 850, 1060 and 1430 cm^{-1} are assigned to a unidentate carbonate. The main point is that no new bands appear after the lean-burn tests and the intensities of the existing bands do not change confirming that no new type of carbonate is formed during exposure to a lean-burn mixture. This behaviour is very similar to barium aluminate and this fact tends to suggest that irrespective of the type of oxide structure that the barium is engaged in, such bonding will protect it against carbonation.

In Fig. 5, the infrared spectra of the three solids exposed to the lean-burn gas mixture at 25°C are displayed. On BaO, three nitrate species could be detected: bands at 1235, 1610 (shoulder) were those of a bridged nitrate, while the band at 1385 cm^{-1} indicates the presence of free nitrates which is a similar form of ionic nitrates [25,26]. Finally, the band at 1270 cm^{-1} associated with a shoulder at 1500 cm^{-1} is a nitrate unidentate. On barium aluminates and $BaSnO_3$, the IR spectra are very similar but the structures of nitrates are completely different to those formed on BaO. Free nitrates still exist with a sharp band at 1385 cm^{-1}, but an N-bound nitrate species (O–Ba–NO_2), with bands at 1360 and 1415 cm^{-1} is unambiguously identified [21,24]. The formation of such a species could be explained by the presence of free oxygen vacancies on barium aluminate or $BaSnO_3$, in which case NO_2 behaves as a Lewis acid and reacts with those vacancies as: $Ba–O+NO_2 \rightarrow O–Ba–NO_2$.

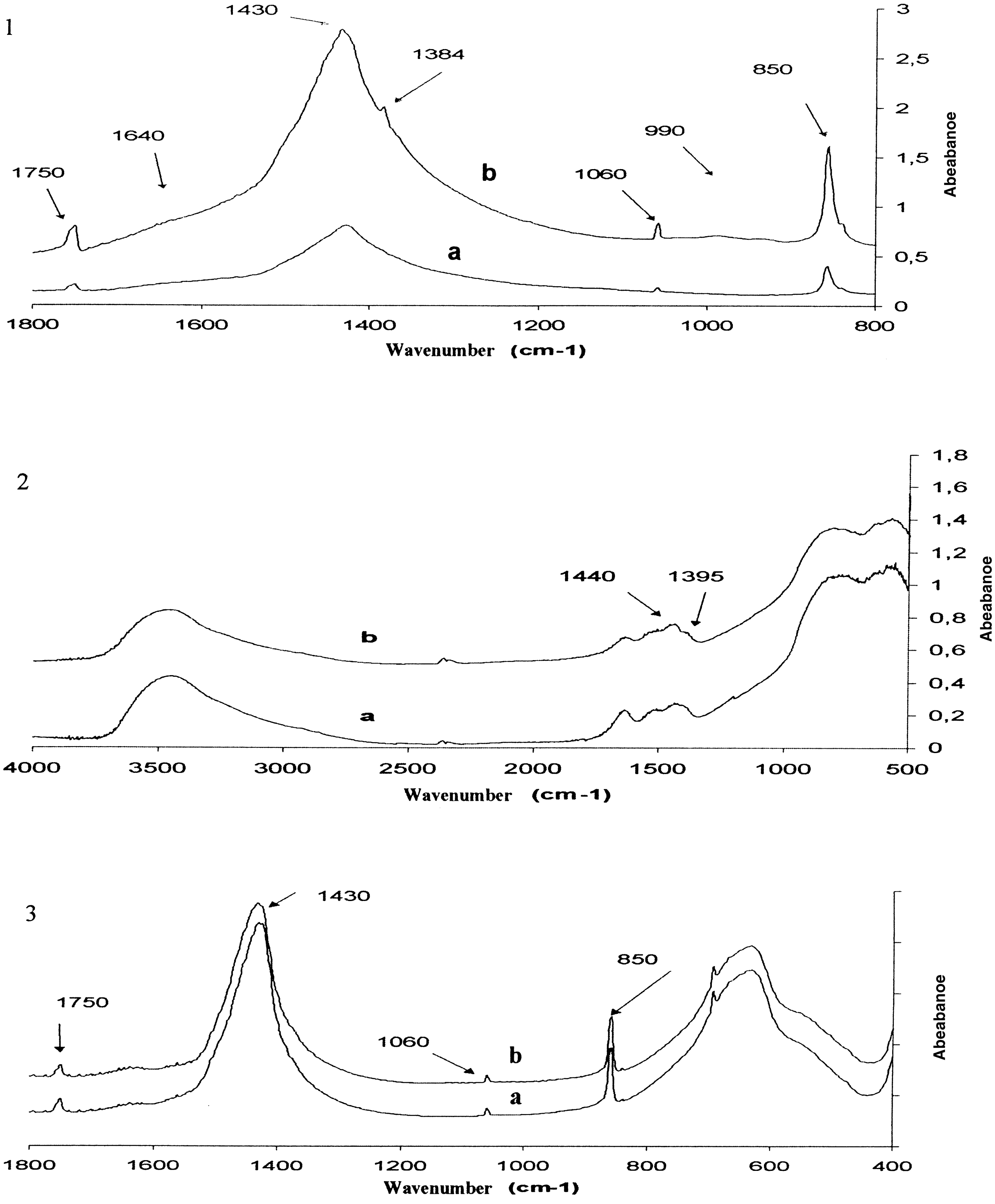


Fig. 4. Comparison of carbonates formation on fresh (a) or reacted (b) form of (1) BaO, (2) Ba aluminate, (3) $BaSnO_3$.

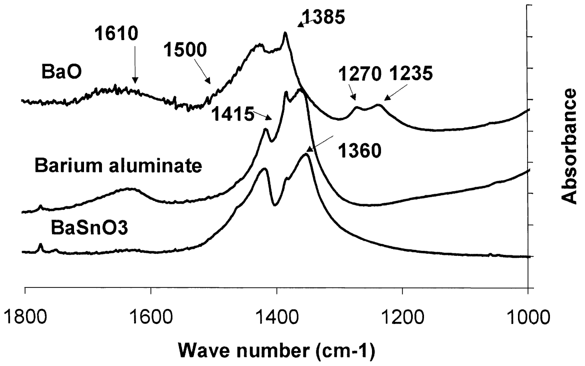


Fig. 5. Infrared spectra on the catalysts saturated with NO_x at 25°C, on BaO, barium aluminate and $BaSnO_3$.

3.3. *Stability of the various species*

Two different sites for these products were clearly identified. In the framework of this study, the formation of nitrates is very important to clarify the nature of the competition between nitrates and carbonates. The stability of each species formed during the NO_x sorption/desorption process was studied by TGA/MS. In this technique, the important parameters to follow are the mass loss, represented as the percentage of the overall mass and the products evolved. They usually result from the decomposition of the species (carbonates or nitrates) formed during the sorption phase. The mass number (*m*/*e*) is representative of the species and the temperature of decomposition of their stabilities. An example is given in Fig. 6a and b. The figure represents the case of the thermogravimetric analysis of $BaSnO_3$ after saturation by NO_x, with the mass loss as a function of the time and temperature (Fig. 6a) and the mass spectrometry analysis of the formed products during the desorption (Fig. 6b).

The overall loss of mass occurring between 25 and 980°C is equal to 7.5%. The mass loss profile reveals three breaks in the gradient, between 100 and 450, 450 and 600 and 800 and 920°C, representing 1.7, 4.5 and 1.3%, respectively. The first of the temperature ranges comprises both the production of water and low temperature carbonates (*m*/*e*=18, 12, 28 and 44). Such a high temperature for water desorption is due to the geometry of the experimental set-up, the water signal is always delayed in time and the maximum of the peak observed at ca. 50 min would normally have been expected at ca. 25 min. The second zone corresponds to the desorption of NO_x shown by the signal *m*/*e*=30. It has to be recalled that the cracking of the NO_2 molecule leads to a ratio of 5–95% for *m*/*e*=46 and 30, respectively. The last region of desorption corresponds to the decomposition of high temperature carbonates materialised by signal at *m*/*e*=12 (C), 28 (CO) and 44 (CO_2).

Table 2 describes all the experiments. In this table the percentage of mass loss is detailed between water, carbonates and nitrates. The procedure of carbonation and nitration are the same as those applied for the infrared study, i.e. three successive lean-burn tests between 80 and 550°C for carbonation or exposure to the lean-burn mixture at 80°C for nitration.

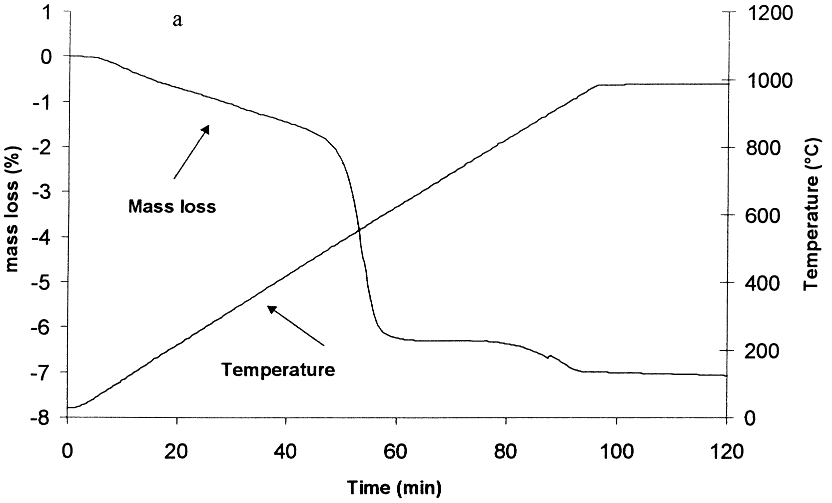
3.3.1. *Fresh samples*

Pure BaO led to a mass loss of 1.9% corresponding to the loss of water and of a small fraction of stable carbonates being decomposed only for temperatures higher than 900°C. With “clean” barium aluminate, the thermogram is very different. The mass loss is 3.9% of which 1.3% is due to water, while the remaining 2.6% which occurs between 200 and 650°C corresponds to carbonate decomposition. On this catalyst, there are no high temperature carbonates.

$BaSnO_3$ underwent a mass loss of 2.6% the first one between 100 and 200°C being due to water the second between 400 and 650°C, and the final one between 650 and 920°C correspond to the decomposition of carbonates having different thermal stabilities. In total, they represent 85% of the overall mass loss.

3.3.2. *Carbonation*

After the carbonation procedure, for BaO, although the temperature of desorption reached was 550°C, there are still some nitrates with a temperature of decomposition of 640°C. These nitrates species are more stable than those formed on barium aluminate and on $BaSnO_3$ since the decomposition of nitrates are completed at this temperature on these latter compounds as proven by the absence of NO signal on the MS signal. This result confirms the one observed during the test of sorption/desorption (Fig. 1). The two other species are carbonates, the overall mass loss is equal to 17%, they represent 14.8% of the mass loss and only the carbonates species with very high stability



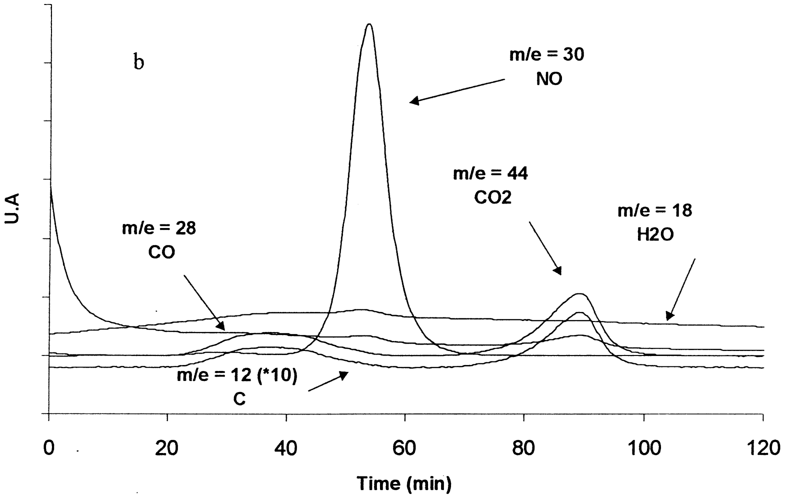


Fig. 6. (a) Thermogravimetric analysis of $BaSnO_3$ previously saturated with NO_x at 25°C under a lean-burn mixture (500 ppm NO, 500 ppm NO_2, 5% CO_2, 10% O_2, 5% H_2O), (b) Mass spectrometry analysis of the product evolved during TGA.

exist, with a temperature of decomposition being higher than 900°C. This clearly explains why the NO_x sorption/desorption process is not reversible with pure BaO under lean-burn conditions. The quantity of very stable carbonate increases run by run, thereby deactivating the sites of nitrate formation. Therefore, the progressive deactivation is explained by the fact that the nitrate sites become gradually occupied by stable and irreversibly formed carbonates after each run. Eventually, all of the sites are taken and complete deactivation is observed. These carbonates cannot be removed even at temperatures in excess of 900°C.

With barium aluminates, the first point to note is that no NO is desorbed, indicating that a temperature of 550°C is high enough to remove completely the nitrates from the sample. The second major difference is that no additional carbonates are formed during the reaction, the mass loss is 4.9% rather than 3.9%, the difference being due to water formed because of the presence of 5% humidity in the stream during the

Table 2

Treatment		Mass loss (%)	Mass loss of each species (T°C of decomposition)		
			Water	Carbonates	Nitrates
Fresh	BaO	1.9	1.7	0.2 (>900)	–
	Barium aluminate	3.9	1.3	2.6 (20–650)	–
	$BaSnO_3$	2.6	0.4	0.5 (400–650), 1.7 (650–920)	–
Carbonation[a]	BaO	17	0	14.8 (>900)	2.2 (640)
	Barium aluminate	4.9	1.4	2.2	0
	$BaSnO_3$	2.8	0	0.35 (400–600), 2.45 (600–920)	0
Nitration[b]	BaO	6.3	0	0.4 (800–920)	5.9 (600–800)
	Barium aluminate	18.8	0	0	13.3 (50–250), 5.5 (330–500)
	$BaSnO_3$	7.5	1.7 (including physisorbed carbonates)	1.3 (800–920)	4.5 (450–600)

[a] Carbonation performed by three successive lean-burn tests between 80 and 550°C.

[b] Nitration preformed by exposure to a lean-burn mixture 3 h at 80°C.

lean-burn test. Moreover, the profile of the TGA is exactly the same before and after three tests, meaning that even after exposure to the exhaust gas mixture, only one type of carbonate is present and that no nitrate sites available upon the surface were poisoned by carbonates as observed with BaO.

For $BaSnO_3$ following three cycles under the lean-burn mixture containing 5% CO_2 (80–550°C), the results reveal an overall mass loss of 2.8%, with the two carbonate species being identical to that observed on the clean solid, i.e. with a temperature of decomposition being comprised between 400 and 650°C for the first one and between 650 and 920°C for the second one. It should be noted that after reactivity, the amount of carbonates formed at high temperature increases at the expense of that formed at low temperature. Nevertheless this variation, like the change in the overall mass loss (difference of 0.2%), is very small. This result clearly reveals that, as for barium aluminate, there are no new carbonate species formed under a reactive mixture containing 5% of CO_2. Therefore, contrary to what is observed with bulk BaO, CO_2 will not affect nitrate formation.

3.3.3. Nitration

On BaO, two regions of desorption are observed. The first one between 600 and 800°C, representing a mass loss of 6.3% and corresponding to the decomposition of nitrates for the first one and the second one above 800°C relating to the degradation of stable carbonates, even present as a percentage of 0.4%.

The barium aluminate fully saturated by nitrates with a lean-burn gas mixture at 25°C underwent an overall mass loss of 18.8% comprising 13.3% for the first peak between 50 and 250°C, and 5.5% for the second between 330 and 500°C. The species desorbed at those temperatures originate only from nitrates. The signal of NO has two regions, which is consistent with the infrared results from which two different nitrate species were identified. For $BaSnO_3$, the overall loss of mass occurring between 25 and 980°C is equal to 7.5%. The mass loss profile corresponding to the decomposition of three species, between 100 and 450°C, 450 and 600°C and 800 and 920°C, represents 1.7, 4.5 and 1.3%, respectively. The first one of the temperature ranges comprises both the productions of water and low temperature carbonates. The second zone corresponds to the desorption of NO_x. The signal of NO_x desorption consists in a very sharp peak confirming the observation made during the standard lean-burn procedure. The last region of desorption corresponds to the decomposition of high temperature carbonates.

Here again, the examination of the analytical results proves that the species formed on barium aluminate and on $BaSnO_3$ are different from those obtained with BaO. The main difference being the formation of carbonates: no carbonates were formed even at room temperature in the presence of 5% of CO_2 on barium aluminates, and the amount of carbonates formed on

$BaSnO_3$ is very small and does not increase above 1.3% even if the time of exposure to the lean-burn mixture is longer than 3 h. This small amount of carbonates on the catalysts, as observed by TGA, is in perfect agreement with the results obtained by infrared.

The work as a whole proves that the electronic environment of barium oxide plays a key role upon its NO_x sorption/desorption properties. Indeed, NO_x sorption on three sorbents presents one common feature which is the fact that only NO_2 and not NO is trapped. But the compounds resulting from this sorption have different structures and different thermal stability. On BaO, high stability carbonates formed during the tests are not decomposed at 550°C leading to a progressive deactivation and a loss of sorbing ability. On the other hand, the exposure of barium aluminate or $BaSnO_3$ to CO_2 does not lead to the formation of carbonates different from those observed on a fresh sample. This fact proves that if barium is engaged in a strong bond with aluminium or tin, it will be protected against carbonation.

The second point of difference concerns the nitrates formation. Both their structure and stability are different. Likewise, if barium oxide is engaged in a chemical bond, two varieties of nitrate are formed, the most abundant resulting from an N-bounded nitrate. This species does not exist on bulk BaO. The formation of such a species could be explained by the presence of free oxygen vacancies on barium aluminate or $BaSnO_3$, in which case NO_2 behaves as a Lewis acid and reacts with those vacancies as: $Ba–O+NO_2 \rightarrow O–Ba–NO_2$. These sites are solely used for NO_2 sorption and not for CO_2, and as a result, the competition between nitrates and carbonates formation is suppressed.

4. Conclusion

The objective of this work was the development of a material able to trap selectively NO_x released from both lean-burn or Diesel engines. Barium contained in a variety of electronic environments in a well-crystallised structure was chosen. The properties towards NO_x sorption/desorption of the family of barium aluminates ($BaAl_2O_4$, $BaAl_{12}O_{19}$) and barium perovskites ($BaSnO_3$) were systematically compared to those of bulk BaO. The main results which stand out of this study are the following:

- NO_2 is the only gas which is trapped in a NO/NO_2 mixture with barium-type trapper. Therefore, the use of barium in a real engine should always include an oxidation function, such as a Pt-containing catalyst before the NO_x absorber device.
- The electronic environment of barium oxide plays a major role upon its sorption properties. The formation of high stability carbonates responsible for a progressive deactivation of BaO could be avoided by including it in a chemical bond. The very different behaviour of bulk barium oxide and barium aluminates and $BaSnO_3$ was explained by the fact that strongly held carbonates are formed on the former which was not the case with the latter, where the competition of formation of nitrates and carbonates is always in favour of the nitrates. Two different sites for these products were clearly identified.

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