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Removal NO_x from Lean Exhaust Gas by Absorption on Oxi-Anionic Materials

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Abstract NO_x sorption/desorption capacities of Oxi-Anionic materials were measured under representative exhaust gas mixture conditions at 300 °C, with a NO_x trap containing CaO and CuO_x impregnated over a commercial γ-Al_2O_3. These systems absorb (or adsorb) NO_x in a gas stream containing both CO_2 at 300 °C. In the case of a thermal desorption, the trapped NO_x should desorb at a temperature below 550 °C.

Keywords NO_x trap · Oxi-Anionic materials · NO_x sorption/desorption · Lean conditions

1 Introduction

Lean-burn gasoline and diesel engines offer the benefits of higher thermal efficiency and lower fuel consumption, thus contributing to the reduction of CO_2 emissions; these engines, however, have some difficulty with NO_x emissions [1, 2]. Due to the surplus of oxygen in their exhausts, NO_x reduction by conventional three-way catalysts (TWCs) is hindered and new post-treatment technologies are required. Without a major advance in catalyst technology, cars using these engines will not be able to meet current and future emission standards.

Most of the previous studies are focused on NO_x reduction in lean conditions like NO_x selective catalytic reduction (SCR) [3–5], Storage and Reduction of the NO_x process (NSR) also referred to as Lean NO_x Traps (LNT) [6–9]; however, other possibilities can be explored to address the emission limits set by the proposed by Tier 4 in the U.S. and Euro IV–V in Europe [10, 11].

The catalysts for the NSR or LNT contain active sites: precious metals (Pt, Rh)—which are expected to oxidize NO to NO_2 and to reduce NO_x—and a storage component containing alkali or alkaline earth metals [6–9]. During lean conditions, NO is oxidized to NO_2 and then stored in the absorbing sites (alkali or alkaline-earth component). A few minutes later, a short pulse of CO, hydrocarbons and H_2 is injected and the nitrate is decomposed to N_2 and H_2O over the surface of precious metals [6–9].

The need for fuel economy and the promising results obtained with NSR and LNT are now attracting many experimental studies aimed at developing this new technology for after treatment of exhausts from lean-burn gasoline engines. Another system for removing NO_x from lean exhaust for diesel, gasoline lean-burn (direct injection engines) and other diluted NO_x gases emissions is the NO_x Adsorber Catalyst (NAC) technology [12–15]. This system can operate in conjunction with diesel particle filters (DPF) to achieve stringent emissions levels [10, 11] with a minimal fuel economy impact. At low temperature the NAC ab(ad)sorb the NO_x and the DPF adsorb soot, while at high temperature the NAC desorbes the NO_x that reaches the DPF burning the soot to produce N_2, CO_2 and H_2O [16–19]. In another case NAC system the nitrate is decomposed and re-circulated the NO_x desorbed to the engine to be thermally destroyed [12].

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Several studies have been devoted to the sorption process [13–15, 20]. They showed that physical adsorption equilibrium is very rapid and reversible (usually it is not specific) while, on the other hand, chemisorption has a specific interaction (with absorption site) and needs energy to form and destroy bonds. Many oxide systems were subjected to NO sorption [14, 15, 20] but, in order to increase storage capacity, it was necessary to oxidize NO to NO_2 with subsequent absorption into alkaline-earth metals [16–19, 21, 22]. The sorption of NO and NO_2 (without noble metals) has also been reported on perovskites containing barium $BaBO_3$ (B = Mn, Fe, Co, Ni) [23, 24] while other authors have also proposed that mixed oxides containing Ba–M (M = transition metal) are active for reversible absorption of NO in an oxidizing atmosphere [14, 15, 21]. These systems should ab(ad)sorb the NO_x in the presence of CO_2 and H_2O in the 25–350 °C temperature range with high space velocity. In the case of thermal desorption, the trapped NO_x should desorb at a temperature below 550 °C [14, 15, 21, 23, 24]. The aim of this paper is to study the activity of new materials for NO_x trap and to evaluate the possibility of a new type of NO_x abatement from a mobile or plant source.

2 Experimental

Sued Chemie Catalysts Italia supplied the oxyanianic material for NO_x trap in powdered form with 0.250–0.600 mm particles.

The $Ca_{0.83}CuO_2$/(γ-Al_2O_3–CaO) material was prepared by incipient wetness impregnation of a commercial γ-Al_2O_3 (271 m^2/g) using at first a nitrate solution containing calcium and then M^{2+} (M^{2+} = Cu and Ca) acqueous solution.

At first an acqueous solution was prepared by suspending by stirring calcium carbonate in demineralised water and slwoly adding 65% nitric acid. The commercial micro-spheroidal γ-Al_2O_3 was impregnated with this solution, left at room temperature for 2 h, dried at 150 °C in the oven overnight and then heated at 750 °C for 3 h. The final composition of the support was (γ-Al_2O_3 + 4.5 wt% CaO. CaO deposited over γ-Al_2O_3 to avoid undesired interactions between binary Ca–Cu oxide ($Ca_{0.83}CuO_2$) and the support.

Then an M^{2+} acqueous solution (Cu/Ca = 0.83 a.r.) was prepared as follows. CuO was mixed with demineralised water, formic acid was slowly added and successively $CaCO_3$. The suspension was heated at 50 °C to favour the complete dissolution of the salts.

The support (γ-Al_2O_3 + 4.5% w/w CaO) was impregnated was impregnated with M^{2+} acqueous solution, after each impregnation the samples was dried at 150 °C overnight. The impregnated material was finally calcined at at 700 °C for 70 h to obtain the Ca–Cu oxide phase ($Ca_{0.83}CuO_2$) [24–26]. The final composition of the absorber was 15% w/w $Ca_{0.83}CuO_2$/(γ-Al_2O_3 + 4.5% CaO) with surface area of 116 m^2/g (measured using Fisons Sorpty 1750).

The absorbing tests were carried out in a quartz reactor at atmosphere pressure using 0.5 g of the sample and a total gas flow rate of 200 mL/min (at 1 atm). The activity of $Ca_{0.83}CuO_2$/(γ-Al_2O_3 + 4.5% CaO) was studied using a series of cyclic sequences of feed changes from:

- sorption conditions (1,000 ppm NO, 0 or 10% CO_2, and 5% O_2 in He)
- to desorption conditions (5% O_2 in He)

The gas hourly space velocity (GHSV) was around 15,000 h^{-1}.

The reactor temperature was set at 300 °C for the sorption step (oxidant phase for 300 s) followed by the desorption step. The desorption temperature started from the isotherm sorption temperature to an higher final temperature (500–700 °C) using a ramp of 10 °C/min. After the desorption process, the sample was cooled down (in He) to 300 °C in order to start a new sorption phase. This cycle was repeated four/five times.

An on-line mass quadrupole analyzer (VG SX200) was used for monitoring the feed composition and reaction products. The NO sorption (in lean conditions) was calculated for each cycle by the formula:

$$\text{NO sorption}(\%) = [(\text{ppm NO}_{\text{inlet}} - \text{ppm NO}_{\text{exit}})/\text{ppm NO}_{\text{inlet}}] \times 100$$

During the desorption process, it was possible to detect the NO_x concentration, determine the quantity of NO_x desorbed, and compare that with the quantity of NO absorbed.

3 Results and Discussion

3.1 NO/He Sorption and Desorption at 500 °C

For the sorption tests, we initially used 1,000 ppm of NO in the presence of 5% of O_2 at 300 °C. Figure 1a reports the NO sorption (%) as a function of time in the four tests.

This sample ($Ca_{0.83}CuO_2$)/(Al_2O_3 + 4.5% CaO), with Cu^{2-3+} [25–27], absorbs NO but, in the first test, the NO sorption dropped rapidly from 93% during the first 60 s to 57% at the end, when the quantity absorbed was low (Table 1). In the following tests (nos. 2, 3 and 4), the

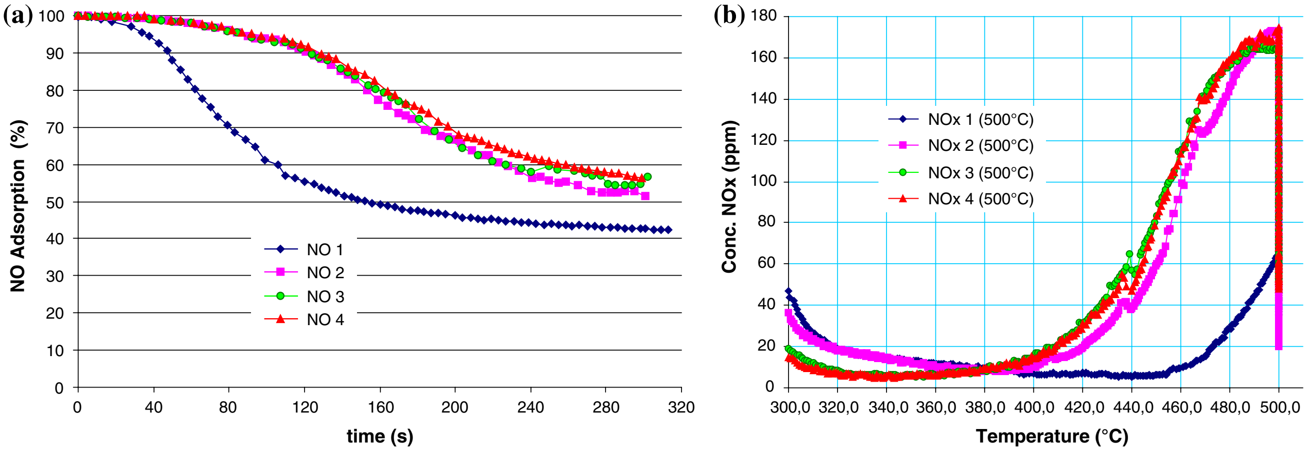

Fig. 1 Sorption/desorption tests for the $(Ca_{0.83}CuO_2)/(Al_2O_3 + 4.5\%\ CaO)$ sample: (**a**) NO sorption (%) at 300 °C; concentration of NO_x getting out of the reactor during a ramp 300–500 °C (10 °C/min) vs. temperature (**b**)

Table 1 Quantity of NO sent, absorbed, desorbed, mean % of NO absorbed and desorbed, during the sorption step at 300°C (with NO/He and NO/CO_2), temperature of initial desorption, and temperature of maximum desorption during the desorption step at 500 or 700°C

Test 300–500 °C NO/He N°	1	2	3	4
mg NO send (S)	1.37	1.39	1.35	1.33
mg NO absorbed (A)	0.78	1.08	1.07	1.08
% NO absorbed (=A/S * 100)	57	78	80	80
mg NO desorbed (D)	0.25	0.43	0.42	0.43
% of NO desorbed (=D/A * 100)	32	40	40	40
Desorption temperature (°C)	460	400	400	400
Desorption temperature of maximum (°C)	>>500	>500	>500	>500
Test 300–500°C NO/CO_2 N°	1	2	3	4
mg NO send (S)	1.30	1.36	1.46	1.34
mg NO absorbed (A)	0.21	0.40	0.45	0.46
% NO absorbed (=A/S * 100)	16	29	31	34
mg NO desorbed (D)	0.17	0.29	0.32	0.31
% of NO desorbed (=D/A * 100)	81	73	71	67
Desorption temperature (°C)	440	400	400	400
Desorption temperature of maximum (°C)	>500	≈500	≈500	490
Test 300–700 °C NO/CO_2 N°	1	2	3	4
mg NO send (S)	1.31	1.26	1.28	1.20
mg NO absorbed (A)	0.51	0.89	0.71	0.92
% NO absorbed (=A/S * 100)	39	70	55	77
mg NO desorbed (D)	0.26	0.53	0.43	0.71
% of NO desorbed (=D/A * 100)	51	60	60	77
Desorption temperature (°C)	440	380	380	380
Desorption temperature of maximum (°C)	540	500	500	490

sample showed a better and more stable activity. In the first 60 s, the NO sorption was around 99% and, at the end of 300 s, around 80%. The sample started to absorb a higher quantity of NO (Table 1). As previously reported [24], the absorption process cannot be limited to the surface but the structure has to open itself during the NO_2 absorption. These results demonstrate that the sample changes the reactivity of storage sites during the cycle of the sorption/desorption process and that the activity stabilizes slowly. The bulk of the structure seems to be changed to produce new chemical species that are more reactive than before. The mechanism of these NAC system involves the NO oxidation over copper ions to form a metal nitrate species. The nitrate ion then shifts to alkaline earth metal because the compound is more stable [14, 15, 18].

After each sorption phase, the temperature was increased up to 500 °C (10 °C/min) in a flow containing O_2 (5%, not reported) in He. Figure 1b shows that the desorption is not complete and that the temperature of 500 °C seems to be too low to have a complete desorption. In the first test, the desorption starts at 460 °C, while for subsequent tests it starts earlier (400 °C); also in these cases, however, the desorption is not complete even after 300 s of isotherm.

The quantity of NO_x desorbed in the first test is around 30%, while for the subsequent tests it is around 40% of NO_x stored. Although the desorption of NO_x was incomplete, the sample maintained the same amount of NO stored. Probably, during the sorption phase, the NO absorbed moved over the surface and inside the bulk, thus reaching stable sites which did not desorb the NO_x. In this way, we can hypothesize that the value of the quantity of NO desorbed was equal to the number of weaker sites present in the catalyst.

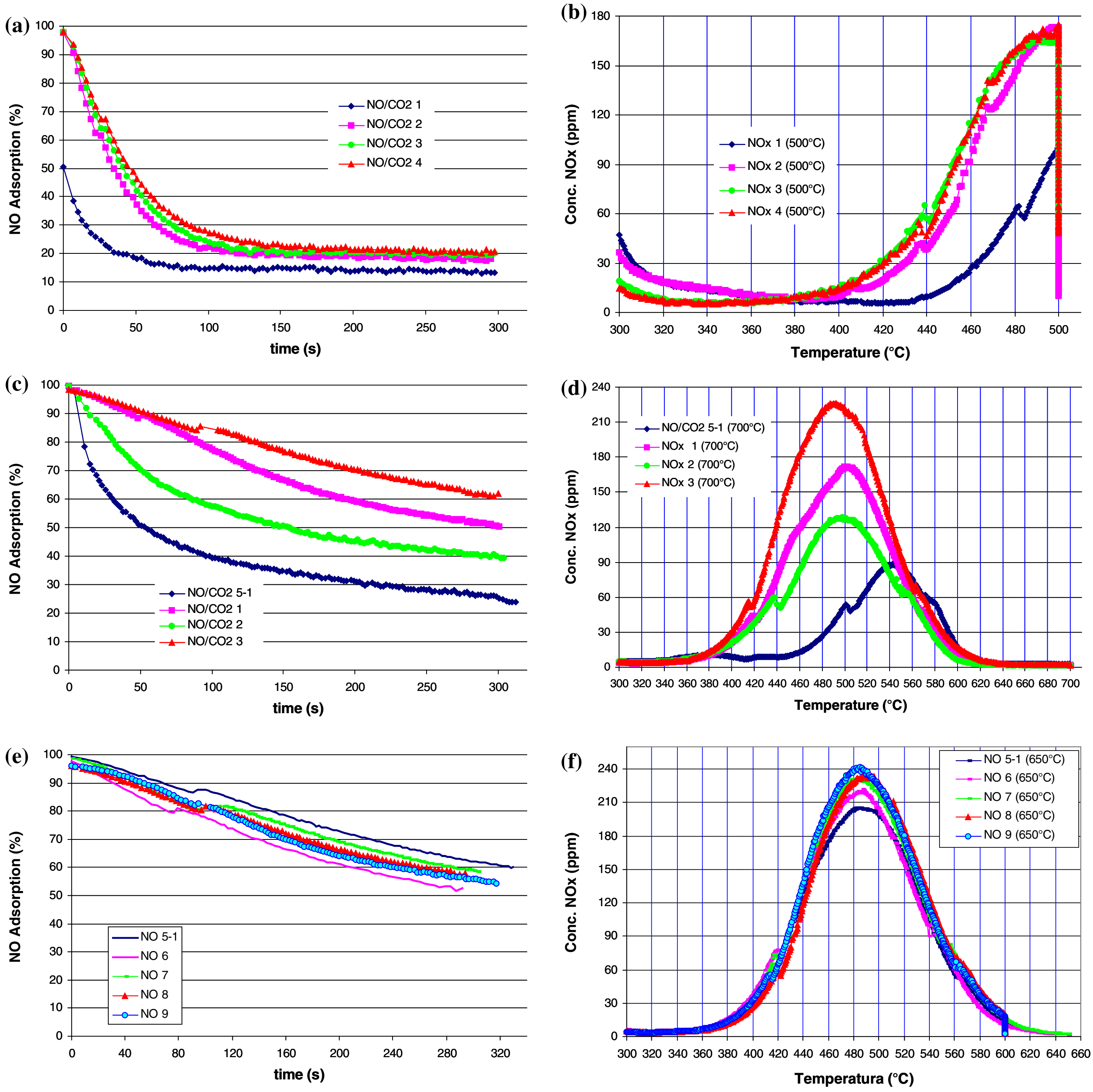

Fig. 2 Adsorption/desorption tests in presence of CO_2 for the $(Ca_{0.83}CuO_2)/(Al_2O_3 + 4.5\%\ CaO)$: (**a**) NO adsorption (%) at 300 °C; (**b**) concentration of NO_x getting out of the reactor during a ramp 300–500 °C (10 °C/min) vs. temperature; (**c**) NO adsorption (%) at 300 °C; (**d**) concentration of NO_x getting out of the reactor during a ramp 300–700 °C (10 °C/min) vs. temperature; (**e**) NO adsorption (%) at 300 °C; (**d**) concentration of NO_x getting out of the reactor during a ramp 300–650 and 300–600 °C (10 °C/min) vs. temperature

3.2 NO/CO_2 Sorption and Desorption at 500 °C or 700 °C

In the presence of CO_2, the sorption capacity of Ca–Cu/γ-Al_2O_3 trap decreased (Fig. 2a) as compared to what was previously reported. In the NSR and NAC catalysis, it is well known that the presence of CO_2 changes the equilibrium $CO_{2,gas} + {}^*NO_{2,stored} \leftrightarrows {}^*CO_{2,stored} + NO_{2,gas}$, thus suggesting the competitive storage of CO_2 and NO_2 for the barium storage sites (*) [7, 14, 15, 28–30]. Therefore, for this sample also, the quantity of NO absorbed in the presence of CO_2 shows the available amount of storage sites. During the storage phase (in the presence of CO_2), the NO cannot easily move over the surface and inside the bulk, and only the most storage sites are reachable.

Some of the previous studies [14, 15, 30] reported that the presence of CO_2 was considered as a poison, because it irreversibly decreases the amount of NO absorbed on samples (especially for samples containing alkaline-earth metals).

The trapping capacity decreased and the NO sorption (in the first test) rapidly dropped from 25% in the first 60 s to 16% at the end of 300 s, thus absorbing a very low quantity of NO (Table 1). In the subsequent tests (nos. 2, 3 and 4), the trapping capacity of the sample increased. In the first 60 s, the NO sorption was around 60% and at the end it was around 30% (Table 1).

The desorption was carried out at 500 °C (10 °C/min) in a flow containing O_2 (5%, not reported) in He.

In the first test, the desorption started at 440 °C (see Fig. 2b), while for the subsequent tests the desorption started earlier (380–400 °C), and in all cases there was a more complete desorption close to 70–80% of the stored NO.

The desorption temperature was changed from 500 °C to 700 °C in order to assess the possible desorption of the entire NO_x stored.

The first test reported in Fig. 2c and Table 1 (actually the fifth test after the fourth desorption at 500 °C) shows an adsorption of approximately 62% in the first 60 s and of 39% in all the tests. During the second test (after the first desorption at 700 °C), the capacity increased and the NO sorption reached 93% and 68%, respectively (0.89 mg of the NO absorbed). The desorption at 700 °C seems to activate a greater number of storage elements, thus leading to higher storage capacity.

The third test was carried out after a “night pause” and registered reduced activity. In the last test (no. 4), the capacity improved significantly, with 0.92 mg of NO absorbed and 97% sorption in the first 60 s. Also in this case, the heating at 700 °C seems to have reactivated the storage elements which were not working during the third test.

During these tests, the $(Ca_{0.83}CuO_2)/(Al_2O_3 + 4.5\%\ CaO)$ reached the same capacity showed in the tests without CO_2, thus demonstrating that the CO_2 is not a poison, but a key factor in a stable process of sorption and desorption.

Figure 2d shows that the desorption seems complete before 560–580 °C. However, in these cases also, the quantity of NO_x desorbed is around 60–70% of the NO absorbed.

Probably, also in the presence of CO_2, during the storage phase the NO absorbed moved over the surface and inside the bulk, thus reaching stable sites that did not desorb the NO_x.

As previously stated, the sample needs some sorption/desorption process cycles in order to increase its activity, but the heating at 700 °C during desorption rapidly increases the trap capacity. It is clear that the structure (bulk and surface) of the sample is unstable and produces new chemical species that are more reactive during the cycles of sorption/desorption before reaching a constant activity.

3.3 NO/CO_2 Sorption and Desorption at 650 °C or 600 °C

The temperature of desorption is a limiting factor because more the temperature is high more energy and time you need to reach a complete regeneration of the sample. The last tests showed that the desorption was complete at temperature lower than 700 °C. For this reason we tried to reduce the temperature of desorption at 650 and 600 °C.

The first test reported in Fig. 2e (actually the fifth test after the fourth desorption at 700 °C) shows an adsorption of approximately 95% in the first 60 s and of 76% in all the tests. After the desorption at 650 °C (test 6 and 7 with desorption at 650 °C), the sample showed the same activity with a NO sorption around 93% and, at the end of 300 s around 74% (0.95 mg of the NO absorbed). After the desorption at 600 °C we obtained the same results reported at 650 °C, with an adsorption around 93% and, at the end of 300 s around 74% (0.95 mg of the NO absorbed).

The desorption at 650 and 600 °C (Fig. 2f) seems to be complete and the same amount of NO_x desorbed is around 90 and 80%, respectively of the NO absorbed and with a maximum temperature desorption around 480–490 °C.

These results confirm that the sample after some cycles of the sorption/desorption (at 700 °C) reaches a stable activity that continues also when the temperature desorption decreases allowing to decrease energy and time necessary to regenerate the sample.

4 Conclusions

The system $(Ca_{0.83}CuO_2)/(Al_2O_3 + 4.5\%\ CaO)$ is able to be a NO_x Adsorber Catalyst (NAC), within a range of temperatures (300–550 °C). The key factors which control the absorption of NO_x seem to be the oxidation over copper (Cu^{2-3+} [25–27]) and the formation of $Ca(NO_3)_2$ [14, 15, 20]. The capacity for NO_x storage is strongly dependent on both CO_2 and desorption temperature. In the presence of CO_2 (with desorption at 500 °C) the storage capacity decreases whereas, when the temperature desorption reaches 700 °C, the storage capacity increases due to the nature of both the bulk and the surface change that creates new chemical species.

Lastly, the repetition of the sorption/desorption cycle strongly affects the process of absorption and desorption by increasing the amount of NO_x trapped and by shifting towards lower desorption temperatures. The influence of the desorption temperature on the sorption/desorption process has not been suggested yet in literature and, therefore, we are going to concentrate our future studies on this aspect.

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