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NO_x storage-reduction catalysts based on hydrotalcite Effect of Cu in promoting resistance to deactivation

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Abstract

Novel NO_x storage-reduction (NO_xSR) catalysts prepared by Pt and/or Cu impregnation of Mg–Al (60:40) hydrotalcite (HT)-type compounds show better performances in NO_x storage than Pt–Ba/Al_2O_3 Toyota-type NO_xSR catalysts at reaction temperatures lower than 250 °C. The presence of Pt or Cu considerably enhances the activity, with the former more active. The nature of the HT source, however, also influences performance. The co-presence of Pt and Cu slightly worsens the low temperature activity, but considerably promotes the resistance to deactivation after severe hydrothermal treatment and in the presence of SO_2. This effect is attributed to both the possibility of formation of a Pt–Cu alloy after reduction, and the modification of the HT induced during the deposition of Cu. The overall Pt–Cu/HT performances are thus superior to those of the Pt–Ba/Al_2O_3 Toyota-type NO_xSR catalysts.

Keywords: NO_x storage-reduction catalyst; Hydrotalcite; Pt; Deactivation

1. Introduction

Fuel-efficient engines such as diesel and lean-burn gasoline engines allow a lowering of CO_2 emissions per kilometre by about 30% with respect to stoichiometric gasoline engines, but the presence of O_2 in the emissions prevents current three-way catalysts (TWCs) from efficiently reducing NO to N_2. Therefore, the objective of lowering noxious gas emissions (NO_x) (as required, for example, in the emission levels proposed by Tier 2 in the US and Euro V in Europe) together with greenhouse gas emissions (CO_2, N_2O) (objective of the Kyoto protocol) requires developing new catalytic solutions to selectively reduce NO to N_2 even in the presence of O_2. The more efficient strategy adopted for this objective was originally developed by the Toyota researchers [1–3], and later also studied by various other research groups [4–10]. These catalysts are based on the concept of storage of NO as nitrate species over the catalyst with periodic reduction of the species by changing the air/fuel ratio (at engine level or by secondary addition of hydrocarbons to the emissions) from oxidising to reducing conditions. The rate of reduction is around two orders of magnitude faster than the rate of storage and therefore the period under rich conditions (excess fuel) is much shorter than the period under lean conditions (excess O_2). The catalysts are usually indicated as NO_x storage-reduction (NO_xSR) catalysts.

The Toyota catalysts are based on the addition of BaO as the NO_x storage component (about 15 wt.%) to a Pt/alumina catalyst [1,2]. Research activity on NO_xSR catalysts [4–10] has been focused on the study of Pt–Ba/alumina materials, while few attempts have been made to search for new types of materials

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to avoid the two main drawbacks related to the use of BaO as the NO_x-storage component: (i) the inhibition effect which barium induces on Pt activity causing low catalyst activity at temperatures lower than 200 °C and (ii) the formation of stable sulphates which requires high temperatures for their regeneration. Periodic high temperature (about 650 °C) regenerations are thus necessary which leads to a considerable fuel penalty and complications in engine management, and especially forms highly noxious H_2S and COS as reaction products. Recent developments by Toyota researchers [3], based on the addition of TiO_2 nanoparticles and Rh/ZrO_2 components to Pt–Ba/alumina catalyst, have led to an improvement in the catalyst regenerability, but temperatures of about 650 °C are still required and H_2S forms as the main reaction product. Furthermore, the first question is not addressed, but is of special interest for emissions from light-duty diesel engines, since a large part of the testing cycle is characterised by low temperature emissions, typically in the 120–200 °C range.

We have reported recently [11,12] that catalyst derived from Mg/Al-hydrotalcite (HT)-type precursors show interesting properties as novel NO_xSR catalysts, especially for the enhanced catalytic properties at low temperatures. The objective of the research reported here was to further analyse these catalysts in comparison with a reference Pt–Ba/alumina Toyota-type catalyst, focusing attention especially on the critical question of resistance to deactivation by SO_2 or under severe hydrothermal treatment and how to limit this deactivation.

2. Experimental

2.1. Sample preparation

HT-based Pt, Cu and Pt–Cu catalysts (1 wt.% Pt, 4 wt.% Cu) were obtained starting from a commercial HT precursor (Mg^{2+}:Al^{3+} = 66:34 as atomic ratio, by CONDEA (D); surface area: 214 m^2/g; preparation by hydrolysis (at $30\,^\circ C < T < 90\,^\circ C$ by an iperstoichiometric amount of water) of a mixture of Mg^{2+} and Al^{3+}-alcoholate) [13] and calcined at 650 °C prior to addition of the Pt or Cu components (sample named HT-C). These were added by incipient wet impregnation with $Pt(NH_3)_2(NO_2)_2$ (sample named Pt/HT-C) and/or $Cu(NO_3)_2{\cdot}3H_2O$ (samples named Pt–Cu/HT-C and Cu/HT-C), where the label C indicates the source of HT. When both Cu and Pt are present, consecutive impregnation is carried out with the noble metal as the final component. The samples are dried and calcined at 550 °C (12 h) prior to the addition of the second component. An alternative commercial source of HT used in the preparations is from ARISTECH (Mg^{2+}:Al^{3+} = 60:40 as atomic ratio; surface area: 201 m^2/g; prepared by reacting a mixture comprising Mg^{2+} and Al^{3+} ions and monocarboxylic anions in an aqueous slurry at $T \geq 40\,^\circ C$ and pH ≥ 7 [14,15] always calcined at 650 °C (sample named HT-A)).

After addition of Pt and/or Cu, the samples were dried at 90 °C overnight, and then calcined at 550 °C for 12 h using a heating ramp of 2 °C/min to reach the final temperature. The final powder was formed in pellets in the 0.250–0.600 mm range which were then activated using a reducing treatment (350 °C for 1 h in a flow of 20% H_2 in He) followed by mild reoxidation (80 °C for 1 h in a flow of air).

The Pt–Ba/Al_2O_3 catalyst (1 wt.% Pt, 15 wt.% Ba) was prepared according to Toyota indications [1–3] by impregnation with Ba-acetate of a Pt/alumina (RP531 γ-Al_2O_3 from rhodia; surface area about 110 m^2/g; Pt (1 wt.%) added by incipient wet impregnation with $Pt(NH_3)_2(NO_2)_2$) (sample name Pt–Ba/Al_2O_3).

2.2. Characterisation and catalytic tests

X-ray diffraction (XRD) patterns were recorded on a Philips PW 1710 instrument using Cu $K\alpha_1$ radiation ($\lambda = 0.15418$ Å, 40 kW, 25 mA). N_2 sorption experiments at 77 K were carried out with a Carlo Erba Sorpty 1750 instrument and specific surface areas (SAs) calculated using the BET method.

Catalytic tests were made in a quartz flow reactor using catalyst loadings in the 0.1–0.5 g range. An on-line mass quadrupole analyser (VG2 lab) was used for monitoring the feed composition and the products of reaction. The mass intensity of the NO (mass 30) and NO_2 (mass 46) was continuously monitored to analyse the NO_x conversion. The conversion to concentrations was made using a periodic switching to a calibrated mixture of NO, NO_2 and N_2O in helium. The absence of formation of N_2O was checked using an on-line FT-IR analyser with a 0.7l volume gas cell. The NO_xSR activity was studied using a series of cyclic sequences of feed changes from lean conditions (120 s: 5% O_2, 10.8% CO_2, 954 ppm NO, remainder He) to rich conditions (6 s: 3.3% CO, 1.1% H_2, 6000 ppm C_3H_6, 5% O_2, 10.8% CO_2, 954 ppm NO, remainder He). The space-velocity was set to 20,000 h^{-1} using the catalyst in the form of powder (30–60 mesh). After evaluating the behaviour during a sequence of cycles (at least 10) at a given temperature, the reactor temperature was raised to another temperature where the behaviour was further monitored in a series of cycles. NO_x storage activity is reported as the mean conversion of NO_x during one cycle, averaged over the series of cycles (at least 10).

Resistance to hydrothermal treatment was checked by comparing the catalytic behaviour in a sequence of cycles before and after a treatment at 800 °C for 24 h feeding air passing in a bubble flask containing water maintained at about 60 °C. The vapour partial pressure at 60 °C is about 0.2 atm, but taking into account of a complete saturation of the feed, it may be estimated that the steam concentration is around 8–10%.

Resistance to deactivation by SO_2 was evaluated using two procedures. The first is based on comparison of the behaviour of the catalyst at 300 °C in a sequence of cycles before and after treatment of the catalyst at 300 °C for 1 h in a flow of 50 ppm SO_2, 5% O_2, remainder He. Then the NO_x storage activity was monitored as above for about 10–15 cycles, after which the reaction temperature was progressively increased up to 500 °C. After around 0.5 h, the reactor temperature was decreased again to 300 °C and the NO_x storage activity evaluated again. This procedure allows the in situ catalyst regenerability to be evaluated during a sequence of NO_xSR cycles at 500 °C.

The second procedure to evaluate the resistance to deactivation by SO_2 is instead based on adding SO_2 directly to the feed during NO_xSR tests and monitoring the change in the mean NO_x conversion (averaged over one cycle) as a function of time-on-stream. In order to accelerate deactivation, in these experiments the concentration of SO_2 in the feed (20 ppm) was about one order of magnitude higher than that typically present in exhaust gas emissions.

3. Results and discussion

3.1. Comparison of HT-based catalysts with the reference Toyota-type (Pt–Ba/Al_2O_3) sample

Compared in Fig. 1 is the catalytic behaviour of HT-C-based catalysts and the reference Pt–Ba/Al_2O_3

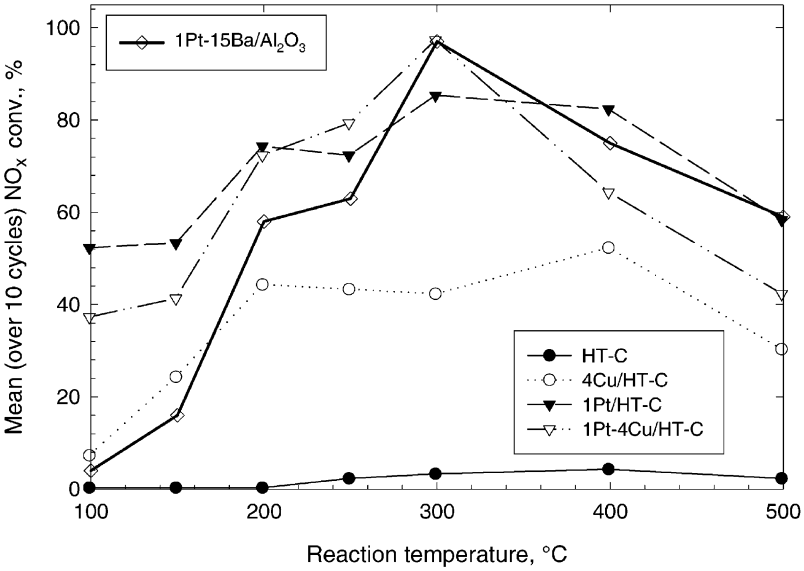

Fig. 1. Effect of the reaction temperature on the NO_x mean conversion (over 10 cycles) of HT-C-based catalysts and the reference Toyota-type Pt–Ba/Al_2O_3 sample.

sample in NO_x storage-reduction, as a function of the reaction temperature in the 100–500 °C range. The following observations can be made:

1. The HT-C matrix itself is inactive in NO storage over the entire range of temperatures examined.
2. All the other samples show a maximum NO_x conversion centred around 300 °C; at low temperatures the maximum may be attributed to a low rate of NO to NO_x oxidation and at high temperatures to thermodynamic stability of NO_x species stored on the catalyst surface.
3. The addition of 4% Cu to HT-C promotes the activity considerably, but the 1Pt/HT sample shows a much higher activity, indicating the more effective activity of Pt in the oxidation of NO to NO_x. The maximum NO conversion in 4Cu/HT-C is around 40–50% with respect to over 80–90% for other samples, apart from HT-C.
4. 1Pt/HT-C, in comparison with 1Pt–15Ba/Al_2O_3 (Toyota-type), shows a much higher activity at low temperatures. In the 100–150 °C temperature range the mean NO conversion of 1Pt–15Ba/Al_2O_3 is about 10% as compared to about 50% for 1Pt/HT-C. However, at 300 °C the conversion of 1Pt–15Ba/Al_2O_3 is 97% as compared to about 80% for 1Pt/HT-C.
5. The addition of 4% Cu to 1Pt/HT-C (1Pt–4Cu/HT-C) slightly decreases activity at low temperatures to about 40%, although remaining higher than that of 1Pt–15Ba/Al_2O_3, and promotes the activity at 300 °C which becomes equal to that of 1Pt–15Ba/Al_2O_3. However, above reaction temperatures of about 400 °C the NO conversion of 1Pt–4Cu/HT-C is slightly worse than that of 1Pt–15Ba/Al_2O_3.

3.2. Role of the HT source

The nature of the starting HT also influences the NO_xSR performance. This is shown in Fig. 2a which compares the behaviour of 1Pt–4Cu/HT samples calcined at the same temperature (650 °C), but prepared starting from the CONDEA (C) or ARISTECH (A) HTs having similar Mg/Al ratios, but different modalities of preparation (see Section 2). The former allows a relevant higher activity at low temperature (100 °C) to be obtained, and the maximum NO_x conversion at 300 °C is higher. The activity however is lower at high temperature (500 °C).

XRD patterns of the HT-C and HT-A samples calcined at 650 °C (Fig. 2b and c, respectively) indicate that the latter sample is characterised by the presence of a much more crystalline MgAl(O) mixed oxide than that obtained from HT-C. Estimation of the mean crystal size of the particles using the Debey–Scherrer formula indicates a mean value of about 20.5 nm for the HT-A sample and a mean value of 4.8 nm for the HT-C sample. When Pt and/or Cu are also present, no changes in the XRD pattern can be noted. This suggests that the crystal size of MgAl(O) mixed oxide, which in turns depends on the thermal treatment and the specific nature of the HT source, also plays a role in determining the NO_x storage behaviour. This observation is consistent with earlier observations on Pt–Ba/Al_2O_3 Toyota catalysts [1–3]. The tentative explanation is that depending on the degree of crystallinity of MgAl(O) mixed oxide, different relative amount of well dispersed Mg(O) species and more bulky Mg(O) species exist. The first species, probably present as surface-like Mg-carbonate, results more active at lower reaction temperatures activity, but less table at higher temperatures, while the second species, probably MgO-type nanoparticles, is less active at lower temperatures, but forms more thermodynamically stable species. The optimal behaviour in terms of wider temperature range requires thus the coexistence of the two type of species.

3.3. Resistance to deactivation by hydrothermal treatment

The resistance to deactivation by hydrothermal treatment at high temperature (800 °C, 24 h, feed of air saturated at RT with H_2O) is an important aspect to analyse, because catalyst temperatures of about 600–700 °C may be reached during full loading operations of engines. The results of these tests are summarised in Fig. 3 which reports the mean NO_x conversion at 300, 400 and 500 °C (averaged over 10 cycles) for 1Pt/HT-C, 1Pt–4Cu/HT-C and 1Pt–15Ba/Al_2O_3 calcined at 650 °C before and after the hydrothermal treatment.

The following observations can be made:

1. The hydrothermal treatment causes a relevant deactivation in all the samples and the maximum

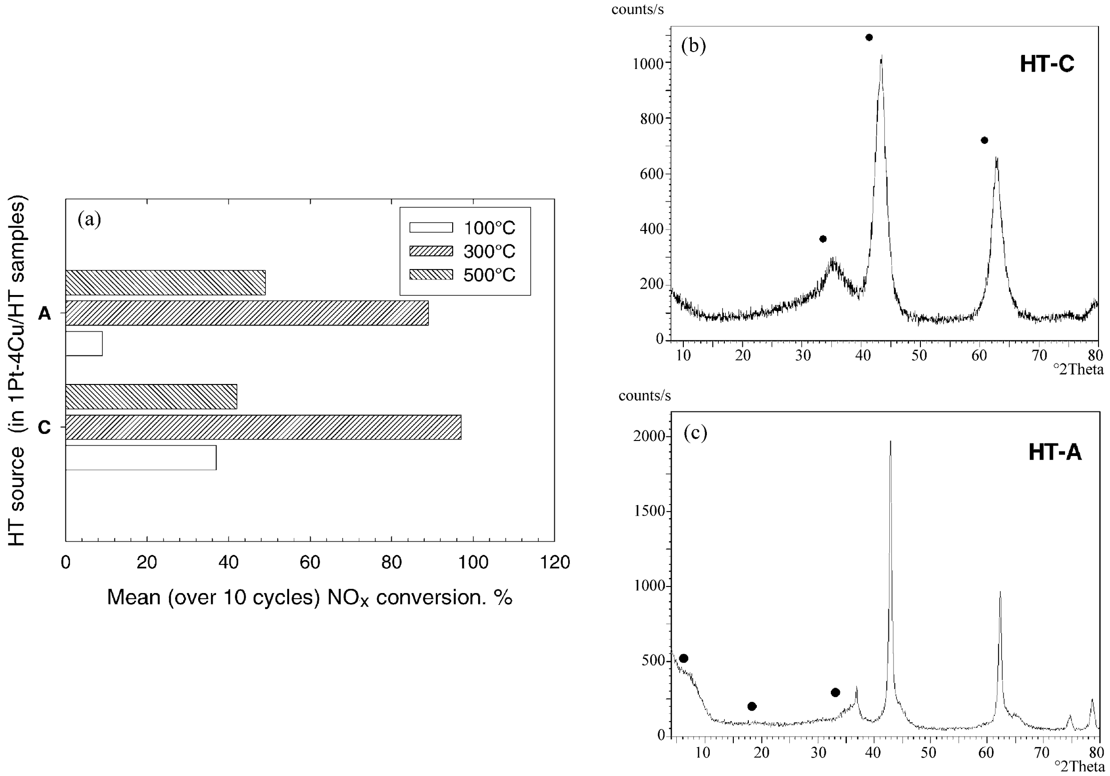

Fig. 2. (a) Role of the HT source on the performance of 1Pt–4Cu/HT samples at three different reaction temperatures. X-ray diffraction patterns of HT-C (b) and HT-A (c) calcined at 650 °C: (▼) MgAl(O) mixed oxide; (●) residual diffraction lines of the starting HT compound.

in NO_x conversion shifts from about 300 to 400 °C. In the reference Toyota-type catalyst (1Pt–15Ba/Al_2O_3) the maximum mean NO_x conversion decreases from about 95% (300 °C) to 64% (400 °C).

2. In 1Pt/HT-C, even more severe deactivation is observed, with a decrease in the maximum mean NO_x conversion from 94% (300 °C) to 31% (400 °C).
3. When Cu and Pt are both present (1Pt–4Cu/HT-C) deactivation after hydrothermal treatment is also observed, but less severe than in the other samples and especially much less severe than in the same samples without copper (1Pt/HT-C). The maximum mean NO_x conversion decreases from about 95% (300 °C) to 77% (400 °C), thus about 15% higher than that observed at the same temperature in the reference Toyota-type catalyst (1Pt–15Ba/Al_2O_3). At 300 °C the mean NO_x conversion is also higher (54% for 1Pt–4Cu/HT-C and 34% for 1Pt–15Ba/Al_2O_3), although at 500 °C the mean conversion is lower due to the lower thermodynamic stability of NO_x on Mg species than on Ba species.

The hydrothermal treatment causes a lowering of the surface area in all samples (Table 1), which, however, is more severe in the HT samples than in 1Pt–15Ba/Al_2O_3. No relevant differences in terms of lowering of the surface area can instead be noted between 1Pt/HT-C and 1Pt–4Cu/HT-C. However, XRD characterisation of these samples before and after hydrothermal treatment (Fig. 4) shows the appearance in 1Pt/HT-C, after hydrothermal treatment, of diffraction lines attributed to crystalline Pt and Mg-aluminate spinel phases. These lines are absent when Cu is

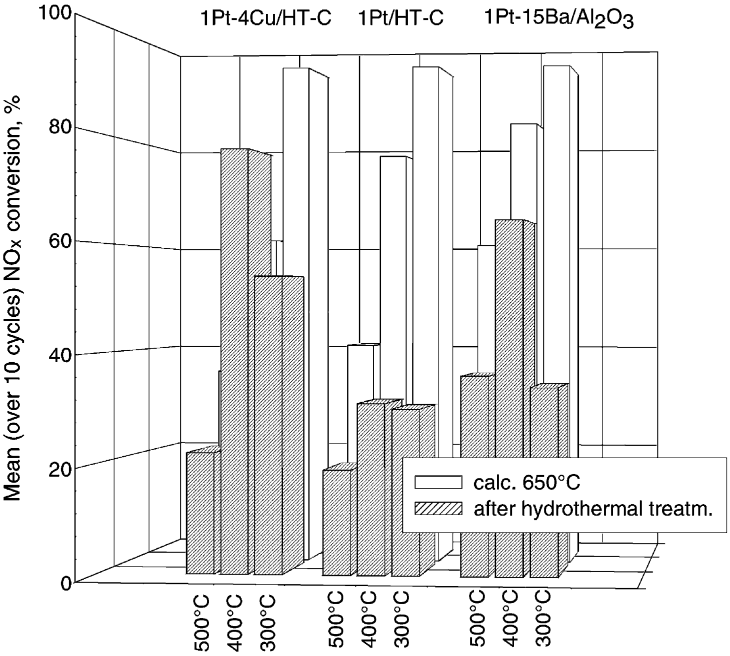

Fig. 3. Comparison of the mean NO_x conversion (over 10 cycles) at different reaction temperatures for 1Pt/HT-C, 1Pt–4Cu/HT-C and 1Pt–15Ba/Al_2O_3 calcined at 650 °C before and after hydrothermal treatment.

present (1Pt–4Cu/HT-C) nor could diffraction lines indicating the presence of copper be detected, notwithstanding the severe hydrothermal treatment which causes rapid sintering of copper in copper-on-alumina samples, for example, when Cu is not stabilised in the form of a surface Cu-aluminate phase [16]. The addition of Cu to HT is made by impregnation in an acid medium and therefore a possible dissolution/reprecipitation of HT may occur, with formation of a Cu-containing spinel-like surface phase after calcination. This may explain why Cu is not detected even after severe hydrothermal treatment and may induce a relevant improvement in the hydrothermal stability of MgAl(O) mixed oxide, avoiding the formation of crystalline $MgAl_2O_4$ spinel. Furthermore, we noted previously that Cu may form Pt–Cu alloys upon reduction in Pt–Cu/HT samples [11,12] and this effect can be responsible for maintaining the Pt more dispersed, thus avoiding severe sintering as noted in 1Pt/HT-C (appearance of crystalline Pt).

Table 1
Surface area of 1Pt–15Ba/Al_2O_3, 1Pt/HT-C and 1Pt–4Cu/HT-C calcined at 650 °C, after hydrothermal treatment and consecutive NO_xSR catalytic tests

Catalysts	Surface area (m^2/g)		
	Fresh	After hydrothermal treatment	After consecutive catalytic tests
1Pt–15Ba/Al_2O_3	110	94	93
1Pt/HT-C	163	105	106
1Pt–4Cu/HT-C	184	109	119

In 1Pt–15Ba/Al_2O_3 no relevant differences are observed in the XRD patterns before and after hydrothermal treatment, apart from the disappearance of reflections due to Ba-carbonate and the parallel appearance of those of BaO.

3.4. Resistance to deactivation by SO_2

The resistance to deactivation by SO_2 is another relevant aspect to consider in developing novel NO_xSR catalysts. This aspect was evaluated using

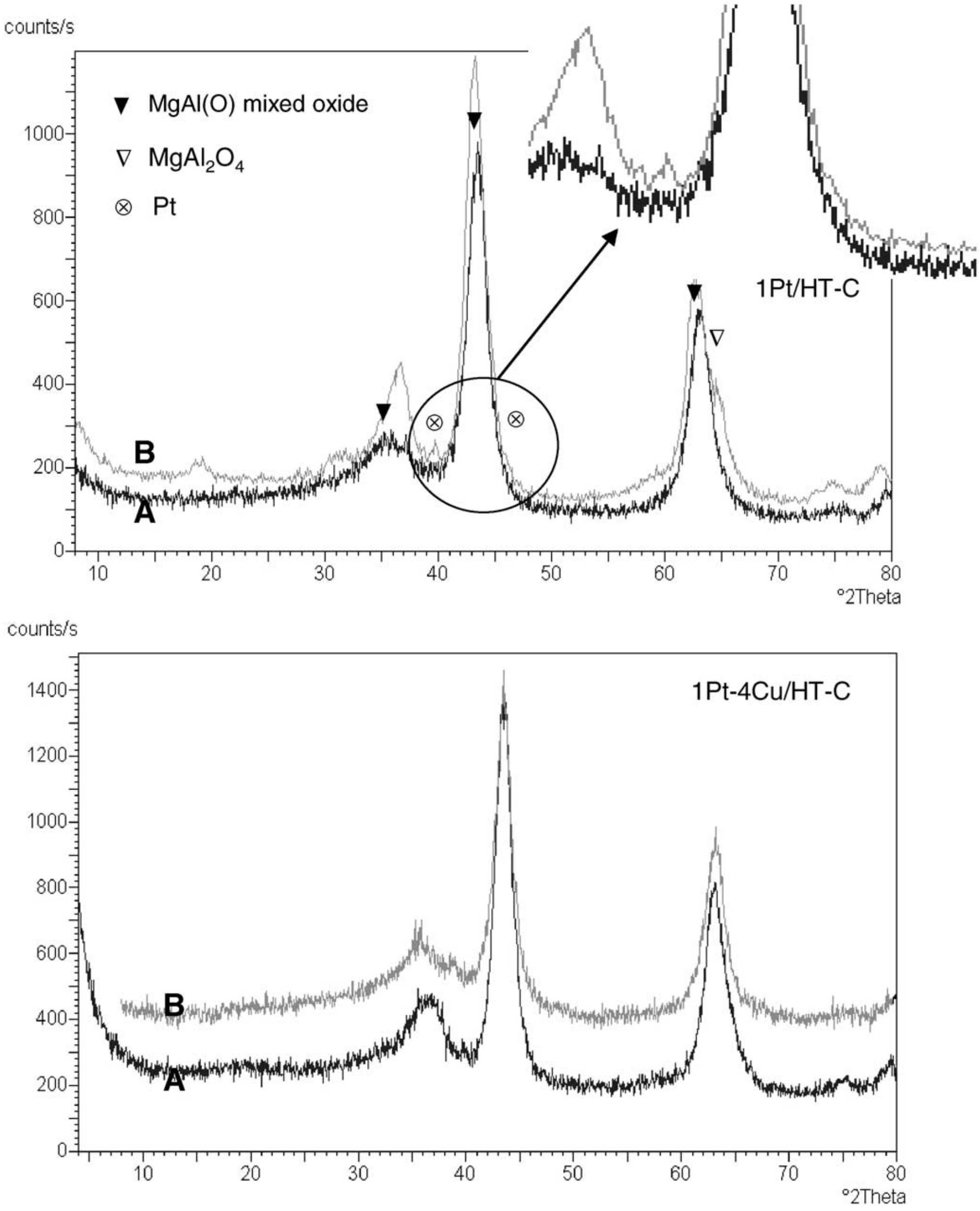

Fig. 4. X-ray diffraction patterns of 1Pt/HT-C and 1Pt–4Cu/HT-C calcined at 650 °C (A) and after hydrothermal treatment (B).

two accelerated procedures for testing deactivation by SO_2, as described in detail in the experimental part. In the first procedure, the catalyst is treated at 300 °C with a flow of SO_2 in air and the catalyst NO_x storage activity is evaluated at 300 °C before and after this treatment. Being also in situ regenerability after SO_2 treatment a relevant parameter to analyse, this aspect is evaluated by making a series of NO_xSR cycles at higher temperature (500 °C) and then again testing the NO_x storage activity at 300 °C. The results are

Table 2
Mean (over 10 cycles) NO_x conversion at 300 °C on fresh catalysts (calcined at 650 °C), after sulphation and after consecutive in situ regeneration

Catalysts	Mean (over 10 cycles) NO_x conversion at 300 °C (%)		
	Fresh	After sulphation[a]	After consecutive in situ regeneration[b]
1Pt–15Ba/Al_2O_3	97	66	97
4Cu/HT-C	42	30	42
1Pt/HT-C	85	82	85
1Pt–4Cu/HT-C	97	89	97
1Pt–4Cu/HT-A	89	79	89

[a] At 300 °C for 1 h; feed 50 ppm SO_2 in air.

[b] In situ regeneration; sequence of NO_x storage-reduction cycles up to a reaction temperature of 500 °C.

summarised in Table 2. The following observations can be made:

1. The treatment with SO_2/air at 300 °C causes, in all cases, lowering of the activity which can be restored completely, however, by in situ regeneration at 500 °C during a sequence of NO_xSR cycles. This suggests that in these conditions surface sulphate species may form, but probably deep sulphation does not occur.
2. Deactivation in 1Pt–15Ba/Al_2O_3 in these testing conditions is quite severe (around 30% loss of activity), while all the HT-based samples, apart from Cu/HT-C, show much less severe deactivation (10% or less decrease in activity). Since the rate of SO_2 to SO_3 oxidation should follow the same trend of NO to NO_2 oxidation, it can be expected that the rate of SO_2 to SO_3 oxidation in 1Pt/HT-C and 1Pt–4Cu/HT-C will be equal or higher than that in 1Pt–15Ba/Al_2O_3, being their

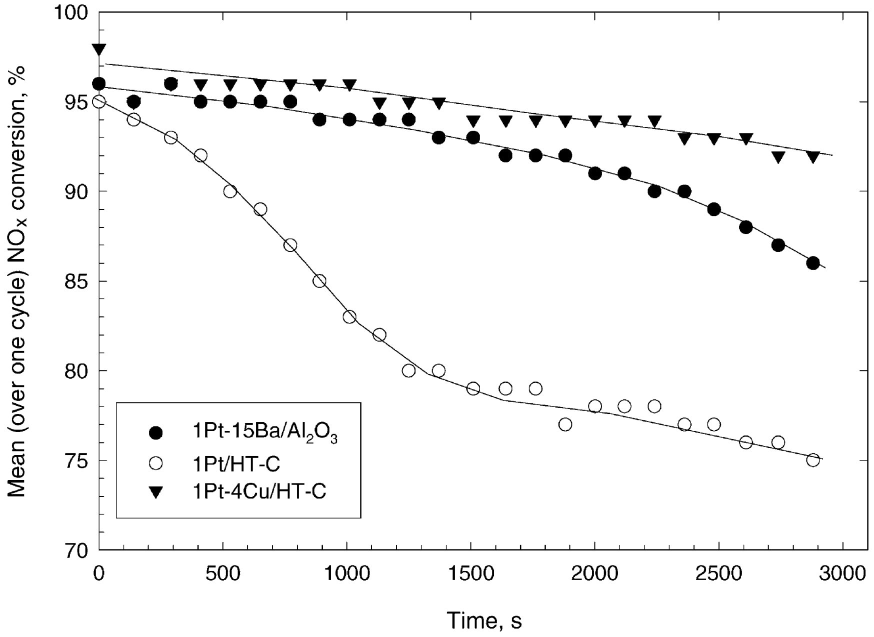

Fig. 5. Mean NO_x conversion (over one cycle) at 300 °C as a function of time-on-stream in NO_xSR tests in the presence of 20 ppm SO_2 in the feed.

rate of NO_x storage below 300 °C (where NO_x storage is controlled by the kinetics of NO oxidation) higher in the HT-based samples than in 1Pt–15Ba/Al_2O_3. Therefore, the lower sensitivity to deactivation of the HT-based samples with respect to the Toyota-type catalyst (1Pt–15Ba/Al_2O_3) may be tentatively ascribed to a lower rate of capture of SO_3 and/or lower stability of surface sulphate species more than to a lower rate of SO_2 oxidation. This aspect, however, requires more study.

The second procedure adopted to accelerate SO_2 deactivation is instead based on adding SO_2 to the feed during NO_xSR tests, although in a concentration around one order of magnitude higher than the typical value present in gasoline engine emissions. The results of these tests for 1Pt/HT-C, 1Pt–4Cu/HT-C and 1Pt–15Ba/Al_2O_3 catalysts calcined at 650 °C are reported in Fig. 5. Fast deactivation of 1Pt/HT-C is noted, differently from the results using the first procedure. Although further studies are required to clarify this question, a possible tentative explanation is the fact that in these tests NO_2, formed by oxidation of NO and not rapidly converted to nitrate, acts as an oxidant for SO_2 (more active than O_2) thus favouring the rate of deactivation. In 1Pt–4Cu/HT-C and 1Pt–15Ba/Al_2O_3 instead the rate of NO_2 to nitrate conversion is faster than the rate of SO_2 oxidation by NO_2, thus limiting this possible mechanism of deactivation.

The presence of Cu in the HT-based catalysts induces a relevant improvement in the resistance to deactivation in the presence of SO_2 in the feed and the resistance to deactivation of this sample is higher than that of the Toyota-type reference catalyst.

4. Conclusions

The analysis of the NO_xSR behaviour of catalysts derived from HT indicates that these materials are interesting novel catalysts for the removal of NO_x from lean-burn gasoline and light-duty diesel engine emissions. With respect to Toyota-type catalysts based on Pt and Ba supported over alumina they allow improved activity at low temperature (lower than 250 °C), although the performance is slightly lower at temperatures above 400 °C. The shift to lower temperatures of the activity curve may be especially important for emissions from light-duty diesel engines which are characterised, for a large part of the testing cycle, by temperatures lower than 200 °C.

The resistance of deactivation under hydrothermal conditions as well as the resistance to deactivation by SO_2 could be significantly promoted in HT-based catalysts by adding Cu which has the probable role of inducing a surface modification creating a Cu-containing surface mixed oxide which stabilises the catalyst against the formation of a $MgAl_2O_4$ spinel phase as well as Pt dispersion by direct copper–platinum interaction which may lead, upon reduction, to the formation of Pt–Cu alloys evidenced by FT-IR characterisation [11,12]. Although the explanation of this stabilisation effect of Cu merits further study, the catalytic effect is clear. The overall performance of the 1Pt–4Cu/HT-C catalyst is higher than that of the reference Toyota-type catalyst (1Pt–15Ba/Al_2O_3) in terms of low temperature activity, resistance to deactivation by hydrothermal treatment and performance stability in the presence of SO_2 in the feed or after sulphation.

Conclusive evidence on the catalytic behaviour of NO_xSR catalysts requires tests on real engines and using catalysts in the form of monoliths. As shown in this work, different catalyst rankings may be observed when the effect of SO_2 is evaluated in the presence or absence of other gas phase components. Similarly, different catalyst rankings may be found in laboratory experiments and those using engine test rigs. Nevertheless, catalysts based on noble metals on MgAl(O) mixed oxides derived from HT and modified by the addition of copper may be considered as novel and promising materials for a new generation of NO_xSR catalysts.

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