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Novel low temperature NO_x storage-reduction catalysts for diesel light-duty engine emissions based on hydrotalcite compounds

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Abstract

A series of Pt and Pt,Cu supported catalysts were prepared by wet impregnation of Mg–Al supports obtained from hydrotalcite-type (HT) precursor compounds. These novel NO_x storage-reduction (NO_xSR) catalysts show improved performances in NO_x storage than Pt,Ba/alumina NO_xSR catalysts at reaction temperatures lower than 200 °C. These catalysts show also improved resistance to deactivation by SO_2. The effect is attributed to the formation of well dispersed Mg(Al)O particles which show good NO_x storage properties. The promoted low temperature activity is explained by the lower basicity of the Mg(Al)O mixed oxide in comparison to BaO, which induces on one hand a lower inhibition on Pt activity (NO to NO_2 oxidation and/or hydrocarbon oxidation) due to electronic effect, and on the other hand a lower thermal stability of the stored NO_x. The presence of Cu slightly inhibits activity at low temperature, although improves activity and resistance to deactivation at 300 °C. On these catalysts FT-IR characterization evidences the formation of a Pt–Cu alloy after reduction.

Keywords: NO_x storage-reduction; Hydrotalcite compound; Diesel light-duty engine

1. Introduction

There is a general consensus that NO_x storage-reduction (NO_xSR)-type catalysts represent the most viable solution for the elimination of NO_x from vehicle emissions containing oxygen (lean burn gasoline and diesel engines), in order to meet future requirements on emissions levels (Tier 2 in the US and Euro V in the European Union). There are, however, two main problems which should be addressed: (i) improve resistance to deactivation by SO_2, in order to minimize the necessity of periodic high temperature (650 °C) regeneration which leads to considerable fuel penalty, forms H_2S as the main S-compound and negatively influences catalyst stability, and (ii) improve low temperature activity in NO_x storage [1–10]. The latter is of special interest for emissions from light-duty diesel engine, since a large part of the testing cycle is characterized by low temperatures of the emissions, typically in the 120–200 °C range.

The NO_x effectiveness of typical NO_xSR catalysts, based on Pt and Ba components supported on alumina (further modified by various additives to improve performances and resistance to deactivation by SO_2), is low at temperatures below 200 °C. In this work it will be shown that novel NO_xSR catalysts derived from hydrotalcite-type (HT) compounds exhibit

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higher NO_x storage activity at temperatures below 200 °C than conventional Pt,Ba/alumina catalysts. The effect of the presence of copper ions, as possible promoter for resistance to deactivation by SO_2 is also reported. Among the parameters able to influence the catalytic performances, we investigated the nature of the metallic phases and the NO_x storage capacity by means of FT-IR spectroscopy.

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 $= 214\,m^2\,g^{-1}$) and calcined either at 650 or 900 °C prior to impregnation by Pt or Cu salts. These were added by incipient wetness impregnation using $Pt(NH_3)_2(NO_2)_2$ or $Cu(NO_3)_2{\cdot}3H_2O$ solutions (samples named Pt/HT_x or Cu/HT_x, respectively), where the subscript x indicates the calcination temperature of the HT support. Pt–Cu catalysts (samples named Pt,Cu/HT_x) were prepared by impregnation of Cu/HT_x samples with $Pt(NH_3)_2(NO_2)_2$ solutions. After each impregnation the samples were dried at 90 °C overnight, and then calcined at 550 °C for 12 h.

The Pt,Ba/Al_2O_3 catalyst (1 wt.% Pt, 15 wt.% Ba) was prepared according to Toyota indications [1–3] by impregnation with $Ba(CH_3COO)_2$ of a Pt/alumina sample (RP531 γ-Al_2O_3 by rhodia; surface area ca. $110\,m^2\,g^{-1}$; Pt (1 wt.%) added by incipient wet impregnation by $Pt(NH_3)_2(NO_2)_2$) (sample named Pt,Ba/Al_2O_3). For comparison, the same sample, but without adding Ba was also prepared (sample indicated as Pt/Al_2O_3).

2.2. Characterization and catalytic tests

XRD patterns were recorded on a Philips PW 1710 instrument using Cu Kα_1 radiation ($\lambda = 0.15418$ nm, 40 kW, 25 mA). N_2 sorption experiments at −196 °C were carried out using a Carlo Erba Sorpty 1750 and the specific surface areas (SAs) calculated using one-point BET method (Table 1). Absorption/transmission IR spectra were run on a Perkin-Elmer FT-IR 1760-X spectrophotometer equipped with a Hg–Cd–Te cryodetector. For IR analysis powders were pelleted in self-supporting discs (10–15 $mg\,cm^{-2}$), activated in vacuum at increasing temperature up to 550 °C, heated in dry O_2 at the same temperature and cooled down in oxygen or subsequently reduced in H_2 at 350 °C and outgassed at the same temperature. IR spectra were recorded at room temperature (RT) before and after interaction with NO (Ucar), NO_2 or with NO/O_2 mixtures and after subsequent evacuation at increasing temperature from RT to 600 °C. NO was freshly distilled before use; NO_2 was prepared by contacting during 2–3 weeks freshly distilled NO with O_2 in excess of the 2:1 reaction stoichiometry and was then purified from O_2 by freezing; the NO/O_2 mixture was prepared in situ by admitting in sequence NO and O_2 ($NO/O_2 = 1{:}4$ v/v).

Table 1
Characteristics of the samples used

Catalysts	Surface area ($m^2\,g^{-1}$)	Crystalline phases (XRD)
Pt/HT_{650}	147	Mg(Al)O
Cu/HT_{650}	128	Mg(Al)O
Pt,Cu/HT_{650}	125	Mg(Al)O
Pt/HT_{900}	98	Mg(Al)O and $MgAl_2O_4$
Pt,Cu/HT_{900}	121	Mg(Al)O and $MgAl_2O_4$
Pt/Al_2O_3	110	γ-Al_2O_3
Pt,Ba/Al_2O_3	110	γ-Al_2O_3 and $BaCO_3$

Catalytic tests were carried out in a quartz flow microreactor using 0.1–0.5 g of catalyst (30–60 mesh powder). An on-line mass quadrupole analyzer (VG2 lab) was used for monitoring the feed composition and the reaction products. The catalytic performances in the NO_xSR were carried out using a cyclic sequence of changes in the feed composition and synthetic mixtures simulating car exhaust emissions in lean (A/F about 18–20) and rich conditions (A/F about 0.95–0.97). Additional catalytic tests were made in steady-state conditions to monitor the catalyst activity in the reduction of NO by propene in the presence of O_2, in order to check the effect of the alkaline-earth component on the reactivity of Pt.

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, remaining 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, remaining He). Space-velocity was set to 20,000 h^{-1}. After evaluating the behavior during a sequence of cycles (at least 10) at a given temperature, the reactor temperature was raised to another temperature where the behavior is further monitored in a series of cycles. NO_xSR activity is given as mean conversion of NO_x during a cycle, further mediated over the series of cycles (at least 10). Resistance to deactivation by SO_2 is evaluated by treating the catalyst at 300 °C for 1 h in a flow of 50 ppm SO_2, 5% O_2 and remaining He. Then the NO_xSR activity was monitored as reported above.

Steady-state catalytic tests were made using the following feed composition: 0.1% NO, 0.1% C_3H_6, 6% O_2 and a GHSV of 50,000 h^{-1}. Tests were made at increasing reaction temperature, waiting for each temperature up to the conversion reached a constant value, usually within 20–30 min.

3. Results

3.1. Catalytic activity in NO_xSR

Compared in Fig. 1 is the catalytic behavior of some HT-based catalysts and the reference Pt,Ba/Al_2O_3 sample in the NO_xSR, as a function of the reaction temperature in the 100–300 °C range before deactivation by SO_2 (Fig. 1a) and in the 300–500 °C range after the deactivation by SO_2 (Fig. 1b). With respect to the reference Pt,Ba/Al_2O_3 sample, the Pt/HT and Pt,Cu/HT catalysts showed a relevant improvement in the NO_x storage activity in the 100–200 °C temperature range. The activity maintained constant over the cycles. At 300 °C the activity of the HT-based samples was comparable to that of reference Pt,Ba/Al_2O_3 sample.

Noticeably, the HT-based catalysts, and particularly that containing Pt and Cu, showed an improved resistance to deactivation by SO_2, although this latter catalyst exhibited the lowest NO_x storage activity at 500 °C. Worth noting is also that the Pt/HT_{900} samples shows a more relevant deactivation that the sample calcined at lower temperature (Pt/HT_{650}) and similarly the NO_x storage activity of Pt/HT_{900} decreases more significantly increasing the reaction temperature than that of the Pt/HT_{650} catalyst.

The reactivity of the catalyst in the reduction of NO_x was tested using the reduction of NO by propene and O_2 as a model reaction. Fig. 2 compares the behavior of Pt/HT_{650} (other HT samples show a comparable behavior) with that of Pt,Ba/Al_2O_3 and of Pt/Al_2O_3. The comparison with the latter sample allows to analyze the effect of BaO or HT support (which contains Mg(Al)O or MgO, Table 1) on the reactivity of the noble metal.

As indexes of the catalytic behavior (Fig. 2) the temperature of maximum conversion of NO ($T_{NO_x\,\mathrm{max\,conv.}}$), the maximum conversion of NO to N_2 (conv. max NO to N_2) and the onset temperature of formation of NO_2 (T_{onset} NO_2) in the tests of NO reduction by propene and O_2 are reported. With respect to Pt/Al_2O_3, the activity of Pt,Ba/Al_2O_3 and Pt/HT_{650} samples is shifted to higher temperatures, although it is less relevant for the HT samples than for Pt,Ba/Al_2O_3. A parallel shift is also observed in the temperature of onset of NO_2 formation, in agreement with mechanistic data pointing out that NO_2 formation is the first step in the reduction of NO by propene and O_2 [11]. This indicates that the presence of Ba inhibits the reactivity of the noble metal towards oxidation of NO to NO_2 and in turns the reactivity of the catalyst in NO_x reduction by hydrocarbons.

3.2. FT-IR characterization

The nature of the Pt phase and the influence of copper on its properties were analyzed by CO chemisorption on samples either oxidized or reduced at 350 °C with H_2. On the oxidized samples (spectra not reported), CO readily reduced at RT PtO to give $Pt^{\delta+}$ carbonyls (2085–2095 cm^{-1}) and mono- and bidentate carbonate species. Notably Pt supported on HT derived mixed oxides or on Ba/Al_2O_3 showed a higher reducibility by CO than Al_2O_3 supported Pt, where Pt^{2+} and Pt^{+} carbonyls were observed (2180 and 2130 cm^{-1}). Summarized in Fig. 3 are the most relevant results obtained upon chemisorption of CO at RT on HT-based prereduced samples. Similar data were obtained for both samples calcined at 650 and 900 °C. On Pt/HT_{650} a slightly asymmetric band centered at 2065 cm^{-1} was observed and attributed to CO linearly bonded on Pt^0 [12]. This band results slightly shifted to lower frequencies with respect to Pt^0 carbonyls on Pt/Al_2O_3 sample

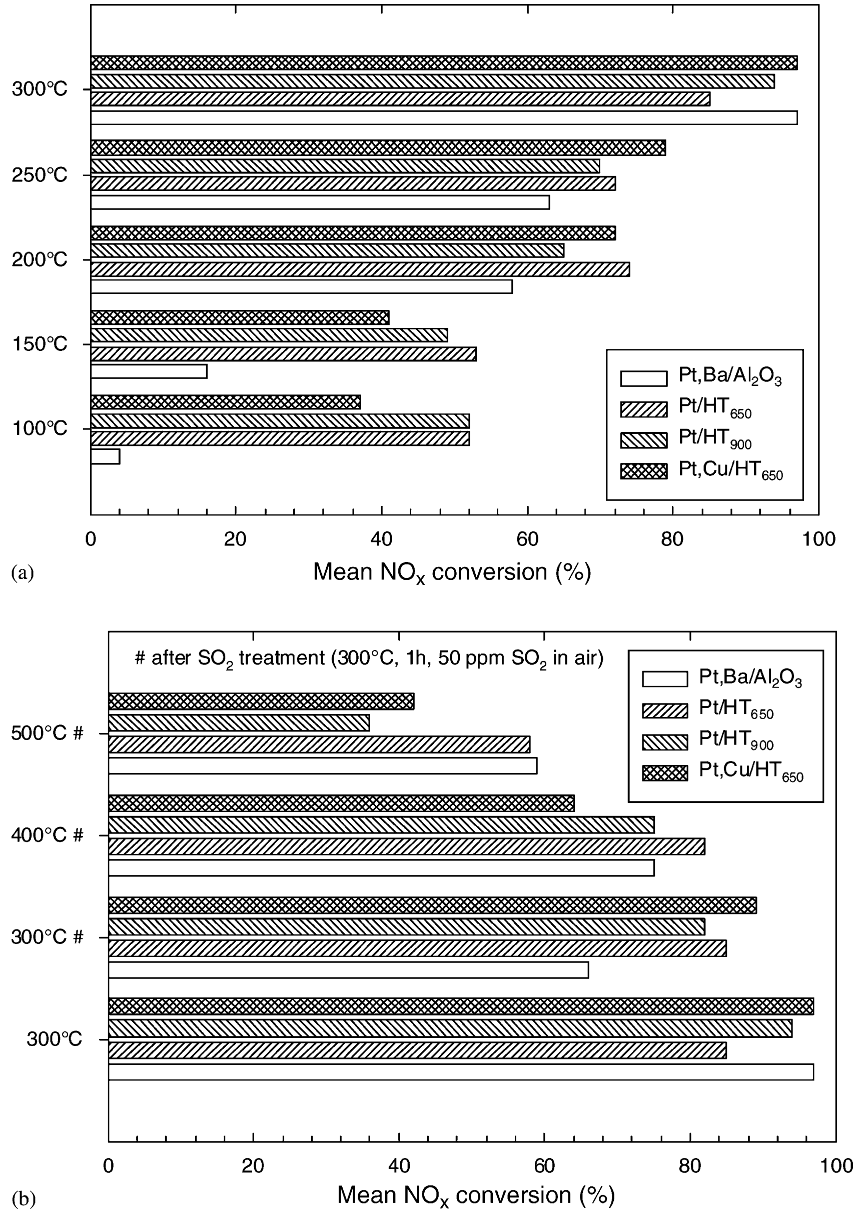

Fig. 1. Comparison of the NO_xSR activity at different reaction temperatures before (a) and after (b) deactivation by SO_2 of HT-based catalysts with respect to a reference Pt,Ba/Al_2O_3 sample.

(bands near 2075–2090 cm^{-1} [13,14]). The effect may be attributed to the greater electron-donor ability of the O^{2-} ions in the HT-derived structure (Mg(Al)O/MgO + $MgAl_2O_4$) compared to alumina increasing the effective charge on platinum particles, with a consequent red shift of the absorption band. However, this effect is lower than that observed for Pt,Ba/Al_2O_3 catalyst where CO linearly chemisorbed on Pt sites with high electron density ($Pt^{\delta-}$) gives bands at 2020 and 1970 cm^{-1} [15].

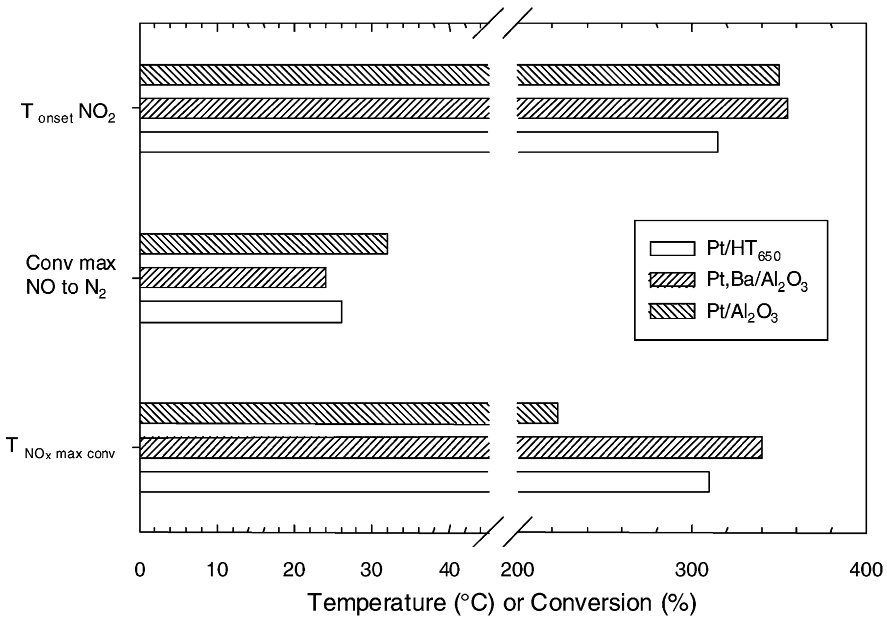

Fig. 2. Comparison of the catalytic behavior in the reduction of NO by propene/O_2 of Pt/HT_{650}, Pt,Ba/Al_2O_3 and Pt/Al_2O_3. $T_{NO_x\ max\ conv.}$: temperature of the maximum in the conversion of NO; conv. max NO to N_2: maximum conversion of NO to N_2; T_{onset} NO_2: onset temperature of formation of NO_2.

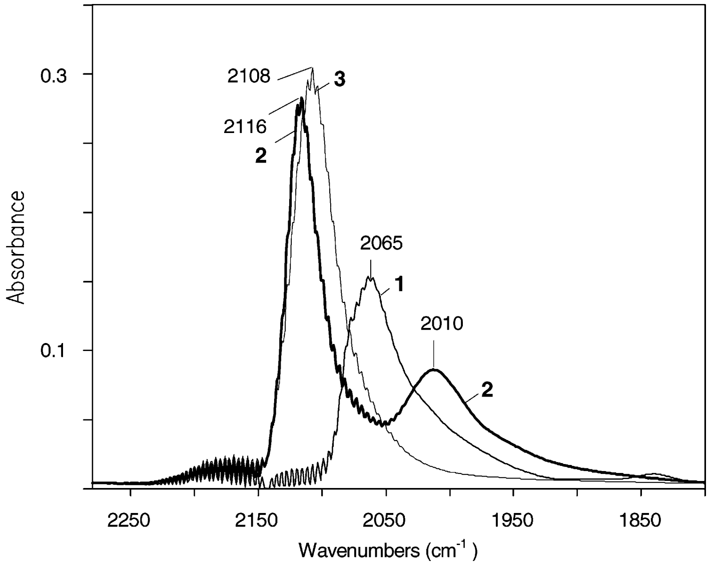

Fig. 3. IR spectra of CO chemisorption (50 Torr) at RT on Pt/HT_{650} (curve 1), Pt,Cu/HT_{650} (curve 2) and Cu/HT_{650} (curve 3) catalysts prereduced in H_2 at 350 °C.

On Pt,Cu/HT prereduced samples the band due to CO linearly bonded on Pt was largely red shifted (from 2065 to 2010 cm^{-1}) with respect to Pt/HT samples, while a blue shift (from 2108 to 2116 cm^{-1}) was observed for the band of CO chemisorbed on $Cu^{\delta+}$ sites with respect to Cu/HT samples. These findings indicate that electron transfer from Cu to Pt atoms occurs, thus increasing the σ donation from CO to Cu and the π back-donation from Pt to CO. A similar behavior has been observed for alumina and silica supported Pt,Cu catalysts and ascribed to the formation of Pt–Cu alloys [16]. As expected, due to the high Cu/Pt atomic ratio in Pt,Cu/HT samples (Cu/Pt = 12), the effect of the charge transfer is larger on Pt than on Cu carbonyls. It is also noted that the band of Pt carbonyls showed lower intensity than on Pt/HT samples. This can be ascribed to the diffusion of a part of Pt from the surface to the bulk of copper particles during the thermal activation of the samples, thus further proving the formation of a Pt–Cu alloy. Indeed, Pt–Cu alloys are reported to form upon annealing to temperatures above 550 K of Cu epitaxially grown on Pt(1 1 1) surface [17].

FT-IR data upon CO chemisorption thus indicate that the presence of basic oxides as well as of copper induce a relevant influence on the surface charge properties of the noble metal.

The NO_x storage ability of the HT-based samples was then studied by FT-IR by analyzing the nature, relative amounts and thermal stability of the surface species formed upon adsorption of NO, NO_2 or NO/O_2 at RT. The results are summarized in Fig. 4 for HT_{650}-based catalysts; similar data were obtained for samples calcined at 900 °C. Upon admission of NO the amount of surface species formed was negligible (Fig. 4a, curve 1 for HT_{650}). Upon admission of freshly preformed NO/O_2 mixtures, ionic nitrites (bands at 1250–1200 and 1330–1320 cm^{-1}, ν_{sym} and ν_{asym}(ONO), respectively) and monodentate nitrites (several overlapped components at 1500–1400 cm^{-1}, ν(N=O), and 1200–1000 cm^{-1}, ν(N–O)) were immediately formed (Fig. 4a, curve 2). On HT, Pt/HT and Pt,Cu/HT samples the amount of nitrite species reached a maximum after 5–15 min of contact with the NO/O_2 mixture and decreased thereafter. On Cu/HT samples nitrites progressively increased up to 40–60 min of contact. Contemporaneously, intense bands assigned to nitrate species developed (Fig. 4a, curve 3). Specifically, bidentate nitrates (bands at 1650–1550 cm^{-1}, ν(N=O), and 1320–1250 and 1050–1000 cm^{-1}, ν_{asym} and ν_{sym}(ONO), respectively) and in minor amounts monodentate nitrates (1500–1400 and 1400–1300 cm^{-1}, ν_{asym} and ν_{sym}(ONO), respectively) were observed. Although it is known that copper forms stable nitrate species [18], due to the heavy band superposition it is not possible to distinguish these species from nitrates bound to the HT support. The same evolution was observed both for the pure HT supports and for Pt and/or Cu-containing catalysts, but for the slower oxidation rate of nitrites to nitrates on Cu/HT catalysts with respect to HT, Pt/HT and Pt,Cu/HT samples.

A different behavior was noted upon admission of NO_2. In this case on all the samples nitrates were immediately formed, while nitrites were not observed (Fig. 4a, curve 4). Nitrates, either formed by adsorption of NO_2 or NO/O_2, showed a high stability upon heating under vacuum: around 15–20% of nitrates present at RT still remained after evacuation at 400 °C (Fig. 4b). This is in agreement with reactivity data (Fig. 1) indicating that catalysts still show NO_xSR activity at reaction temperature above 400 °C, although markedly decreased.

Both the nature and thermal stability of the NO_x surface species were not significantly affected by the presence of Pt and/or Cu supported phases, nor by the calcination temperature of the HT supports (650 or 900 °C) and the catalyst pretreatment (oxidation at 550 °C or reduction in H_2 at 350 °C). At variance, the amount of stored NO_x decreased in the order HT $\approx$ Pt/HT $\geq$ Pt,Cu/HT $>$ Cu/HT (Fig. 4c). This trend was observed both for the HT_{650} and HT_{900} series, but it may be probably attributed to a change in the surface acid–base properties occurring during the addition of Pt and Cu components by impregnation, confirmed by FT-IR results upon acetonitrile adsorption (to be published). In particular, the acidic $Cu(NO_3)_2$ solution may induce local effects of redissolution and reprecipitation and of reconstruction of HT structure. However, the presence of CO_2 (about 11%) in the reaction mixture in the NO_xSR tests in flow reactor probably makes uniform the differences observed in the acid–base properties.

In conclusion, FT-IR results indicate that the NO_x storage ability and the nature of the NO_x stored species depend mainly on the composition of the gas phase

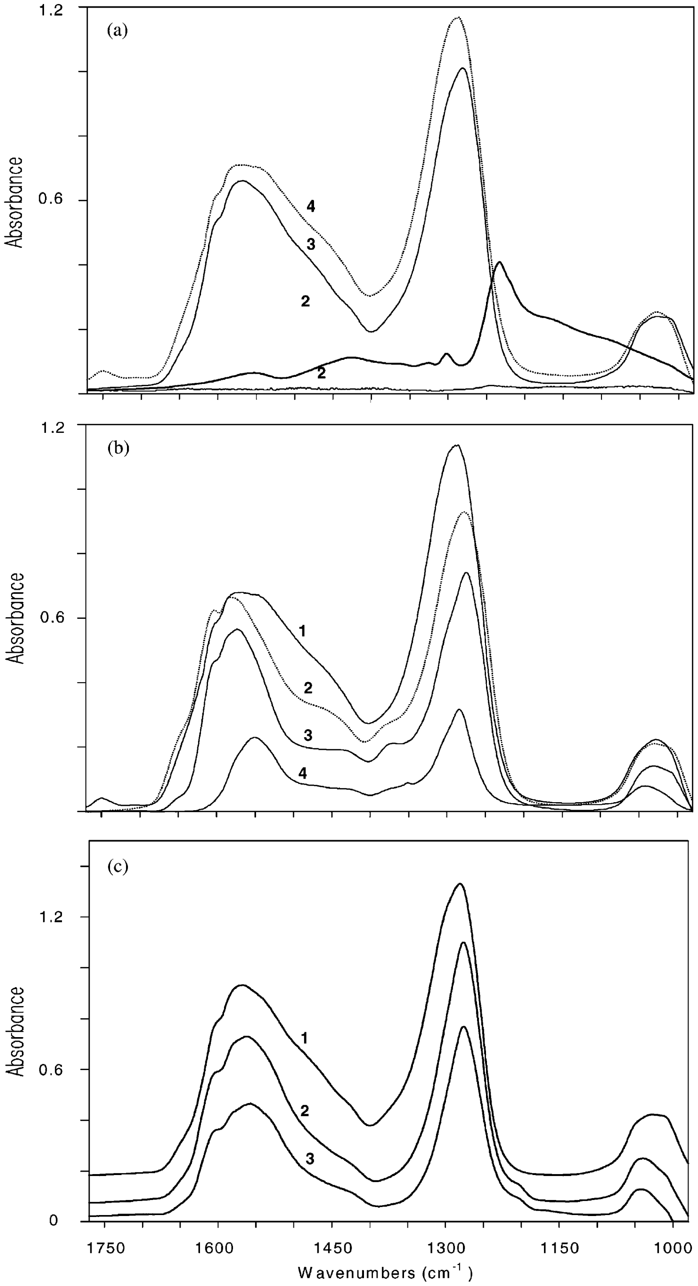

Fig. 4. IR spectra upon interaction with NO, NO/O_2 and NO_2. (a) Admission of NO (5 mbar) on HT_{650} (curve 1); NO/O_2 (20 mbar, NO/O_2 = 1:4 v/v), spectra recorded after 5 min (curve 2) and 30 min of contact (curve 3); NO_2 (5 mbar), spectrum recorded after 5 min of contact (curve 4). (b) Admission of NO_2 (5 mbar) on HT_{650} (curve 1); subsequent evacuation at 423 K (curve 2); 573 K (curve 3) and 673 K (curve 4). (c) Admission of NO/O_2 (20 mbar, NO/O_2 = 1:4 v/v) on Pt/HT_{650} (curve 1); Pt,Cu/HT_{650} (curve 2); Cu/HT_{650} (curve 3), spectra recorded after 120 min of contact. Each spectrum is reported as a difference with the spectrum before admission of the gas (NO, NO/O_2 or NO_2, respectively).

admitted, while not on the presence of Pt or Cu. The spectra of stored NO_x species on HT-based samples are very similar to those found on Pt,Ba/Al_2O_3 samples [10], pointing out that the Mg–Al mixed oxides (Mg(Al)O/MgO + $MgAl_2O_4$) have a similar role than Ba/Al_2O_3 in the storage of NO_x.

4. Discussion

Data reported in Fig. 1 show clearly that HT-based catalysts exhibits a promoted low temperature ($\leq$200 °C) NO_xSR activity as well as a better resistance to deactivation by SO_2 than reference Pt,Ba/Al_2O_3 catalyst, although worsen performances at the higher temperatures of reaction (500 °C). The presence of also Cu in the catalyst does not have an overall considerable effect: it promotes slightly the resistance to deactivation and activity at 300 °C, but worsens behavior at lower and higher temperatures. Reactivity data in the conversion of NO_x by propene/O_2 indicate that Ba inhibits the reactivity of Pt in the oxidation of NO to NO_2 and/or in the hydrocarbon activation, due to the strong electronic interaction of the alkaline-earth ion with the noble metal, evidenced by FT-IR data. In particular, the NO oxidation to NO_2 has been usually considered being the first step in NO_x storage and determined from the presence of Pt particles [5–8]. However, we noted that HT support itself (without Pt) show a high activity at low temperatures in the storage of NO_x, result confirmed also by FT-IR evidences (Fig. 4). The amount of stored NO_x on the HT support is comparable to that of Pt/HT. These findings suggest that the noble metal plays a major role in the NO_x reduction, while the NO oxidation is mainly governed by the oxygen activation on the oxidic support. Further studies are in progress to clarify this aspect.

The fact that Pt,Ba/Al_2O_3 shows a lower activity below 200 °C than the HT-based samples (which progressively tend to segregate MgO on increasing the temperature of calcination [19]) may reasonably explained considering their different basicity. As observed by Katoh et al. [2], decreasing electronegativity decreases the amount of stored NO_x (due to lower thermal stability), but increases the rate of hydrocarbon oxidation, also an index of the inhibition effect of alkaline metals on Pt reactivity. Magnesium has an electronegativity of 1.31 versus 0.89 for barium, thus MgO has a lower inhibition effect on the noble metal, in agreement also with the data of Fig. 2. Therefore, HT-based materials show a promoted low temperature activity.

No relevant differences are observed between Pt/HT_{650} and Pt/HT_{900} at temperatures up to 400 °C. At variance at higher temperatures ($\geq$400 °C), Pt/HT_{900}, which is characterized by large MgO particles (unlike Pt/HT_{650} in which a slightly crystalline Mg(Al)O mixed oxide is present, see Table 1), show worse performances. This can be ascribed to the larger dimension of the MgO particles influencing the high temperature stability of the stored NO_x species or alternatively to the fact that in Pt/HT_{900} reconstruction of HT structure in the presence of water and CO_2 (see below) could be more difficult than in Pt/HT_{650}.

The nature of the oxide support also determines the resistance to deactivation by SO_2. Accordingly, the HT supported catalysts showed a better resistance to deactivation in comparison to reference Pt,Ba/Al_2O_3 catalyst due to the lower basicity of the Mg(Al)O mixed oxides. Moreover, Pt/HT_{650} shows a less relevant decrease of the activity at 300 °C after treatment with SO_2 than Pt/HT_{900} (Fig. 1b).

HT-based catalysts show therefore interesting properties as novel NO_xSR catalysts and may be expected a further improvement of their properties, being possible an easy change of their characteristics, which depend on the Mg/Al ratio and the presence of other elements in the structure [19]. A further characteristic of these materials is the possibility to reconstruct the HT structure during catalytic reaction due to the “memory effect” in the Mg(Al)O mixed oxides [19] especially in the presence of the high water and CO_2 concentrations typical of the emissions from car engines. This property may be very important to maintain a high dispersion of the alkaline-earth oxide and avoid deactivation especially upon severe hydrothermal treatment.

In conclusion, HT materials are a new route to prepare NO_xSR catalysts with improved low temperature activity properties as well as stability properties, taking into consideration also the great flexibility possible in their preparation which allows introducing in a homogeneous way other components which could further improve overall properties of these samples.

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