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A study of the behaviour of Pt supported on CeO_2–ZrO_2/Al_2O_3–BaO as NO_x storage–reduction catalyst for the treatment of lean burn engine emissions

L.F. Liotta[a,*], A. Macaluso[b], G.E. Arena[c], M. Livi[d], G. Centi[c], G. Deganello[a,b]

[a] *ISMN-CNR Via Ugo La Malfa, 153, 90146 Palermo, Italy*
[b] *Dipartimento di Chimica Inorganica, Università di Palermo viale delle Scienze, 90128 Palermo, Italy*
[c] *Dipartimento di Chimica Industriale ed Ingegneria dei Materiali, Università di Messina, Salita Sperone 31, 98166 Messina, Italy*
[d] *Dipartimento di Chimica Industriale, Università di Bologna, V.le Risorgimento 4, 40136 Bologna, Italy*

Abstract

The behaviour of a Pt(1 wt.%) supported on CeO_2–ZrO_2(20 wt.%)/Al_2O_3(64 wt.%)–BaO(16 wt.%) as a novel NO_x storage–reduction catalyst is studied by reactivity tests and DRIFT experiments and compared with that of Pt(1%)–BaO(15 wt.%) on alumina. The former catalyst, designed as a hydrothermally stable sample, is composed of an alumina modified with Ba ions and an overlayer of ceria-zirconia. The results pointed out that during the calcination barium ions migrates over the surface of the catalyst which thus show a good NO_x storage–reduction behaviour comparable with that of Pt–BaO on alumina, although Ba ions result much better dispersed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Pt supported catalyst; Storage–reduction catalyst; Lean burn engine emissions

1. Introduction

Lean burn or diesel engines are characterized by lower fuel consumption and CO_2 emissions than current engines operating at a stoichiometric air/fuel ratio, but the presence of oxygen in their emissions prevents the use of current three-way type catalysts. It is thus necessary to develop catalysts or new solutions which allow reducing NO_x to N_2 in engine emissions containing oxygen.

Solid adsorbents are attracting considerable attention for the application to car emissions and other flue gas treatment processes in oxidising atmosphere [1]. Researchers at Toyota [2,3] have developed a catalytic system based on the concept of NO_x storage–reduction (NO_xSR). The key features of this approach are the presence of a NO_x storage compound (usually BaO) and the use of cyclic changes in the feed composition from lean to rich conditions, but with the latter period being usually 50–100 times shorter than the lean period.

There is a good agreement that these NO_xSR catalysts are one of the most promising solutions for lean burn and light duty diesel engines [4], but critical aspects are the fast deactivation by SO_2 and the insufficient hydrothermal stability. Being Ba- and Al-sulphate species minimally reducible during the rich period reducible during the rich period of the cycles up to temperatures of about 550 °C, periodic regeneration at higher temperature (about 650 °C) are necessary. This causes severe fuel penalty and lowers drivability of the car (the time for this

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[*] Corresponding author. Tel.: +39-091-6809361;
fax: +39-091-6809399.
E-mail address: liotta@ictpn.pa.cnr.it (L.F. Liotta).

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high-temperature treatment may be as long as 60–120 s); furthermore, H_2S forms as the main product of sulphate reduction. The high hydrothermal stability is required to avoid catalyst deactivation during this periodic treatment and during full load operations of engines. A main effect typically observed after severe hydrothermal treatment is a reduction of the activity in NO_x removal at low temperature. A good activity below 200 °C is very important for overall catalytic converter performances, because the temperature of the emissions in typical procedures for checking auto-exhaust emissions is below 200 °C for over 50–60% of the testing time.

Recent advances on the composition of these NO_xSR catalysts are the introduction of titania nanoparticles and of Rh/ZrO_2 components to improve the regeneration during the periodic high-temperature treatment in rich conditions [5,6], but the question of resistance to deactivation by SO_2 and hydrothermal stability are not solved. It is thus necessary to develop new materials which combine a very high hydrothermal stability, a good activity at low temperature and a good resistance to deactivation by SO_2.

Commercial three-way catalysts usually contain ceria or ceria–zirconia as oxygen-storage component to improve performances in the presence of oscillations in the air to fuel ratio around the stoichiometric value [4]. The characteristics of ceria–zirconia with respect to ceria are the very high hydrothermal stability and its positive role in promoting dispersion of Pt and Rh noble metals [7]. Alumina high-temperature resistance characteristics may be promoted by the addition of alkaline-earth metals during the preparation [8]. A support composed by zirconia–ceria on Ba-modified alumina (CeZr/AlBa) is thus a suitable candidate to develop NO_xSR materials having high-temperature resistance. Furthermore, (i) the ceria may also act as NO_x storage component in lean conditions and can play a role in promoting reduction in rich conditions, (ii) ceria–zirconia has a good resistance to deactivation by SO_2, (iii) zirconia promotes gas shift reaction during high-temperature treatments in rich conditions (H_2 produced by gas shift reaction improves regeneration of sulphate [6]), and (iv) a high dispersion of Ba by inclusion in a alumina matrix would limit the formation of bulk-type $BaSO_4$, promoting its reducibility during the "normal" cyclic operations (i.e. for temperatures of the emissions below about 500–550 °C).

There are thus a number of reasons which indicate that CeZr/AlBa is an interesting support for NO_xSR catalysts. However, a basic question is whether or not Ba remains in the bulk of alumina or tend to migrate on the surface of alumina or even of ceria–zirconia surface layer and thus this material itself may be used as NO_x storage–reduction catalyst upon Pt addition, i.e. without further addition of BaO.

The aim of the present work is a preliminary investigation of a Pt(1 wt.%) supported on CeO_2–ZrO_2(20 wt.%)/Al_2O_3(64 wt.%)–BaO(16 wt.%) sample by reactivity tests, NO-TPD and in situ DRIFT experiments in comparison with reference Pt(1%)/Al_2O_3 and Pt(1%)/Al_2O_3–Ba(20 wt.%) samples, in order to clarify above questions as well as to identify analogies and differences in the behaviour.

2. Experimental

2.1. Catalyst preparation

All the used reagents (Aldrich) were of analytical grade. The support $Ce_{0.75}Zr_{0.25}O_2$(20 wt.%)/Al_2O_3 (64 wt.%)–BaO(16 wt.%) mixed oxide was prepared in two steps by a sol–gel method. The choice of this procedure was based on previous findings about the advantages of the sol–gel approach which provides pure, reproducible, homogeneous and high thermally resistant materials [9]. Al_2O_3(80 wt.%)–BaO(20 wt.%) mixed oxide was synthesized according to a published procedure dealing to alumina xerogel resistant to high-temperature calcination treatments [10]. Barium acetylacetonate, aluminium-*sec*-butoxide in isobutanol, ethyl acetoacetate for complexation were used as starting materials. Water, close to stoichiometry for hydrolysis, and a small quantity of ammonia were added. Gelation took place in a thermal bath at 95 °C. The system dried at 100 °C overnight was calcined up to 950 °C for 4 h. The resulting alumina–baria has a BET surface area of 135 m^2/g.

Synthesis of $Ce_{0.75}Zr_{0.25}O_2$ solid solution was accomplished by using as precursors zirconium *n*-propoxide dissolved in *n*-propanol and cerium nitrate dissolved in ethanol; the addition of water in excess immediately leads to the hydrolysis of the mixture and the formation of a pseudo-gel. $Ce_{0.75}Zr_{0.25}O_2$(20 wt.%)/Al_2O_3(64 wt.%)–BaO(16 wt.%) sample was obtained by impregnation of the alumina–baria with the appropriate amount of the ceria–zirconia gel. The resulting suspension evaporated to dryness in vacuum was calcined at two different temperatures, 650 °C for 8 h and 950 °C for 4 h in order to stabilize the ceria–zirconia solid solution.

The catalyst Pt(1 wt.%) on $Ce_{0.75}Zr_{0.25}O_2/Al_2O_3$–BaO, indicated hereinafter as Pt–CeZr/AlBa, was prepared by impregnation of the mixed oxide with a solution of $Pt(acac)_2$ in toluene at 70 °C. After drying under vacuum, the solid was calcined at 500 °C for 5 h and then reduced at 350 °C for 5 h.

The Pt(1%)/Al_2O_3–Ba(15 wt.%), indicated as Pt–Ba–Al hereinafter, was prepared using as support γ-Al_2O_3 impregnated with a solution of $Ba(CH_3COO)_2$, dried at 80 °C and calcined at 500 °C for 5 h. The platinum was added by the same procedure as before.

The preparation of other reference samples not containing Ba, namely Pt(1 wt.%) on alumina (indicated as Pt–Al_2O_3 hereinafter) and Pt(1 wt.%) on ceria–zirconia supported on alumina (indicated as Pt–CeZr/Al_2O_3 hereinafter) was reported elsewhere [11], but follows basically the procedure indicated above, although using commercial alumina (γ-Al_2O_3 from Rhone–Poulenc, surface area 110 m^2/g).

2.2. Characterisation

The X-ray diffraction pattern of Pt–CeZr/AlBa catalyst was recorded with a Philips apparatus using nickel filtered Cu Kα radiation. Diffraction peaks were fitted by using a pseudo-voight function and the crystalline phases were identified by comparison with the ICDD files. BET surface area and pore size distribution measurements were performed by using a Sorptomatic 1900 Carlo Erba instrument. Temperature-programmed reduction (TPR) studies were carried out on a Micromeritics 2910 instrument equipped with a thermal conductivity detector (TCD), the experiments were performed under 5% H_2/Ar with a constant flow rate of 30 ml/min, heating from room temperature to 1000 °C (rate, 10 °C/min). All the TPR experiments were made on the samples calcined at 500 °C for 5 h (these samples are indicated as fresh ones). To minimize the contribution from adsorbed species, before each run, the samples were treated in Ar (30 ml/min) at 500 °C for 2 h. In situ DRIFT studies have been made using a Specac environmental diffuse reflectance chamber mounted on a Bruker Equinox 55 spectrometer with an MCT detector.

2.3. Catalytic tests

The pretreatment of the catalysts before the catalytic tests was made in situ in the reactor, following this procedure: calcination flowing 5% oxygen in helium at 500 °C for 1 h, in order to clean the surface, reduction at 350 °C in 20% H_2/He for 1 h, cooling to 200 °C in pure He, then reoxidation at 200 °C in a flow of 5% O_2/He for 1 h. The same procedure was also for DRIFT studies.

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 100,000 h^{-1} using the catalyst (0.1 g) in the form of powder (30–60 mesh). After evaluating the behaviour during a sequence of cycles (at least 20) at a given temperature, the reactor temperature is raised to another temperature where the behaviour is further monitored in a series of cycles. The feed and reactor outlet composition was monitored by an on-line mass quadrupole apparatus.

The steady-state activity in the reduction of NO to N_2 in the presence of C_3H_6 in oxidizing conditions was studied in a flow reactor apparatus equipped with on-line mass quadrupole and a GC for full analysis of the feed and products composition. Mass intensity data were corrected to account for mass overlapping. The amount of catalyst was 0.1 g and the total flow rate (STP) was 100 ml/min, equivalent to a space velocity of about 50,000 h^{-1}. A thermocouple in contact with the catalytic bed allowed the control of the reactor temperature. The feed composition for the tests was 0.1% NO, 0.1% C_3H_6, 5% O_2, 94.8% He. The steady-state tests were made at increasing reaction temperature, waiting for each temperature that the conversion reaches a constant value, usually within 20–30 min.

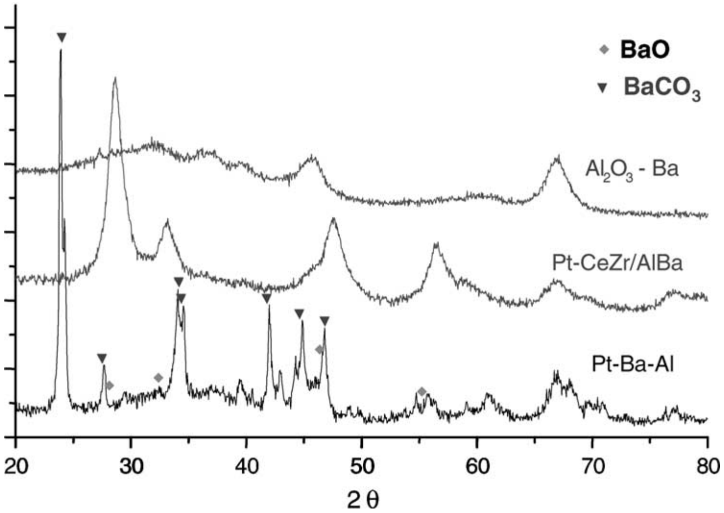


Fig. 1. Experimental XRD patterns of the Al_2O_3(80 wt.%)–BaO(20 wt.%) oxide calcined at 950 °C and of the supported catalyst Pt–CeZr/AlBa, calcined at 500 °C and reduced at 350 °C for 5 h. For comparison the XRD pattern of Pt–Ba–Al sample is also shown.

3. Results

3.1. Characterisation of the samples

Fig. 1 shows the powder XRD patterns of the alumina–baria, calcined at 950 °C and the catalyst Pt–CeZr/AlBa after calcination at 500 °C and reduction in H_2 at 350 °C for 5 h. The pattern of alumina–baria displays a nearly fully amorphous structure. On the contrary, the structure of the catalyst Pt–CeZr/AlBa appears more crystalline and characteristics reflections peaks of a fluorite-like structure can be observed. Crystalline phases were identified by comparison with the ICDD. The most intense peak at $2\theta = 28.89^\circ$ was assigned to the solid solution $Ce_{0.75}Zr_{0.25}O_2$, accordingly, the calculated lattice parameter $a = 5.3525$ Å, compares well with the literature value $a = 5.3490$ Å [12]. The broad shape of the peaks is indicative of the good dispersion of the ceria–zirconia crystallites over the alumina–baria support. The absence of reflections peaks at 39.7 2θ due to the Pt metallic could be attributed to the high dispersion of the metal.

For comparison, the XRD pattern of Pt–Ba–Al sample is also shown in Fig. 1. Differently from two previous cases, sharp diffraction lines are present in this samples which could be attributed to the presence of BaO and $BaCO_3$, with the latter being predominant. This is in agreement with previous observations and indicates that upon exposure to air BaO readily transforms to a carbonate species. The complete absence of such a XRD diffraction lines in Ba–Al_2O_3 and Pt–CeZr/AlBa samples (confirmed by Rietvel analysis) indicates that either Ba is absent from the surface of these samples or is present in a form which prevents its reaction with gaseous CO_2.

Fig. 2 shows the TPR profiles of the fresh samples such as $Ce_{0.75}Zr_{0.25}O_2$(20 wt.%)/Al_2O_3(64 wt.%)–BaO(16 wt.%) oxide and the supported Pt catalyst. The presence of the metal appears to favour the reduction of the support. A H_2 consumption of 0.28 mmol/g has been measured for the peak at 130 °C. This value is higher than 0.1 mmol/g, expected for the reduction of all Pt^{IV} to Pt^0 indicating that the reduction peak at 130 °C is a concomitant reduction of α-[PtO_2] species highly dispersed [13] and partially a surface reduction of the ceria support. The peak at 600 °C is associated with a further reduction of Ce^{4+} species and at 790 °C the reduction of the bulk occurs. The observation that ceria reduction occurs at lower temperatures in the sample containing Pt indicates that Pt is present, at least in part on the surface of ceria–zirconia, while the absence of detection of a reduction peak for Pt supported on alumina (which occurs at higher temperature than 130 °C) suggests that ceria–zirconia is effectively well dispersed over alumina, forming

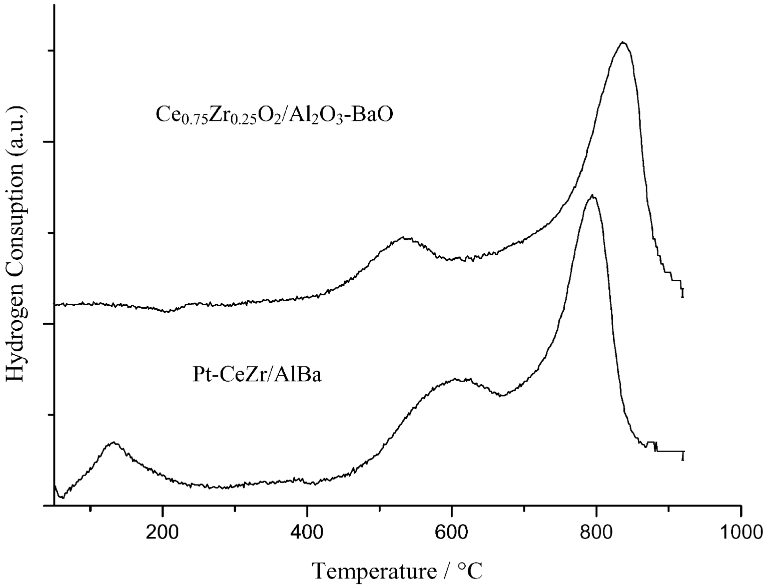


Fig. 2. TPR of the fresh samples: CeO_2–ZrO_2(20 wt.%)/Al_2O_3(64 wt.%)–BaO(16 wt.%) and Pt–CeZr/AlBa.

a complete layer on it. This observation is further confirmed by scanning electron microscopy measurements which reveal a well-homogeneous distribution of Zr and Ce in the sample and the absence of detectable regions where only alumina is present.

Worth noting the TPR profile of Pt supported on ceria–zirconia on alumina (thus without the presence of BaO) calcined at 1000 °C show a main reduction peak (related to ceria reduction) centred around 400 °C [11]. This indicates that there is a shift in the ceria reduction, reasonably associated to the presence of surface Ba ions. This is confirmed by SEM–EDAX analysis. While the mean Ba/Al ratio determined by EDAX analysis increases a factor about 2, increasing the calcination temperature from 650 to 1000 °C, relevant changes in the distribution map of Ba are not detected. This fact indicates that no segregation of phases occurs, but only a homogeneous surface enrichment in Ba. Further studies are in progress to better demonstrate this conclusion.

3.2. Reactivity towards NO_x conversion

Reported in Fig. 3 is the behaviour of Pt–CeZr/AlBa catalyst in NO_x storage–reduction experiments. These tests were made at high space velocity (100,000 h^{-1}) in order to better evidence the reactivity of only surface species and thus obtain data more reliable with respect to application. The tests were typically made using a sequence of cyclic changes in the feed composition from lean conditions (120 s) to rich conditions (6 s). Feed (see Section 2) contains about 10% CO_2, 0.1% NO, 5% O_2 (during lean period) or a mixture of CO, H_2 and C_3H_6 (rich period) with composition equivalent to those of emissions having an air to fuel ratio of approximately 0.95–0.97. The reactor outlet concentration of NO during the lean period in one cycle at different reaction temperatures is reported in Fig. 3. After the initial fast adsorption, the rate of NO_x storage progressively decreases and tends to stabilizes after about 100 s, being adsorption in these conditions mainly determined from diffusion rate. By increasing the reaction temperature, the NO_x storage decreases, being the surface nitrate less stable. This behaviour is typically observed in NO_xSR catalysts.

The amount of NO_x stored in 120 s/mg of catalysts of Pt–CeZr/AlBa is compared in Table 1 with that of Pt–Ba–Al. The behaviour of Pt–CeZr/AlBa sample in NO_x storage during cyclic lean–rich changes in feed composition is quite comparable with that of reference Pt–Ba–Al samples over the temperature range analysed.

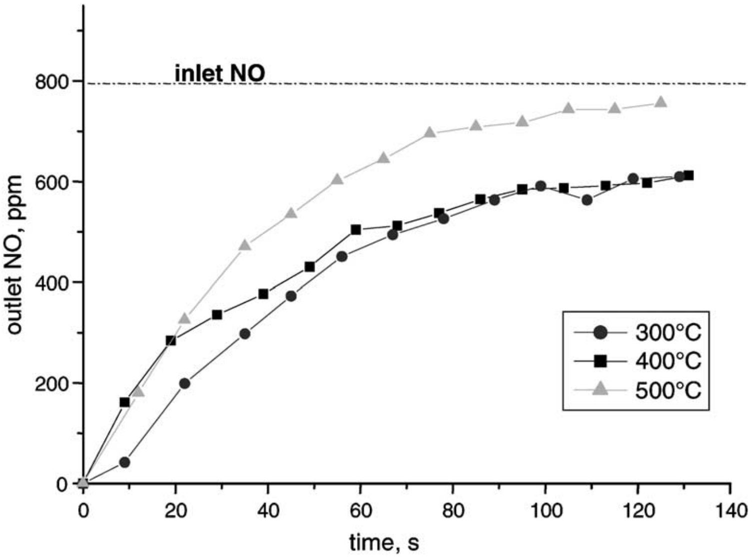


Fig. 3. Reactor outlet concentration of NO during the lean period for CeZr/AlBa in one cycle at different reaction temperatures.

Table 1
Moles of NO_x stored in 120 s/mg catalysts and as a function of the reaction temperature during one cycle (lean period) in NO_xSR experiments

Catalyst	300 °C	400 °C	500 °C
Pt–CeZr/AlBa	7.2×10^{-8}	6.6×10^{-8}	3.3×10^{-8}
Pt–Ba–Al	8.1×10^{-8}	7.1×10^{-8}	5.1×10^{-8}

In order to further analyse the surface reactivity, the steady-state activity of Pt–CeZr/AlBa in the reduction of NO by propene, in presence of oxygen, was also analysed and compared with that of the other samples. These reactivity data are summarized in Table 2. As indexes of the catalytic behaviour, the following parameters are reported: temperature of maximum NO conversion (T_{max}) and relative maximum NO conversion (NO_{max}), selectivity to N_2 at the temperature of maximum NO conversion ($S_{N_2\,max}$). The catalytic behaviour of Pt–CeZr/AlBa is compared with that of Pt–Ba–Al as well as with that of reference samples not containing Ba (Pt–Al_2O_3 and Pt–CeZr/Al_2O_3).

Table 2
Comparison of the catalytic behaviour in NO reduction by propene in the presence of O_2 over different catalysts

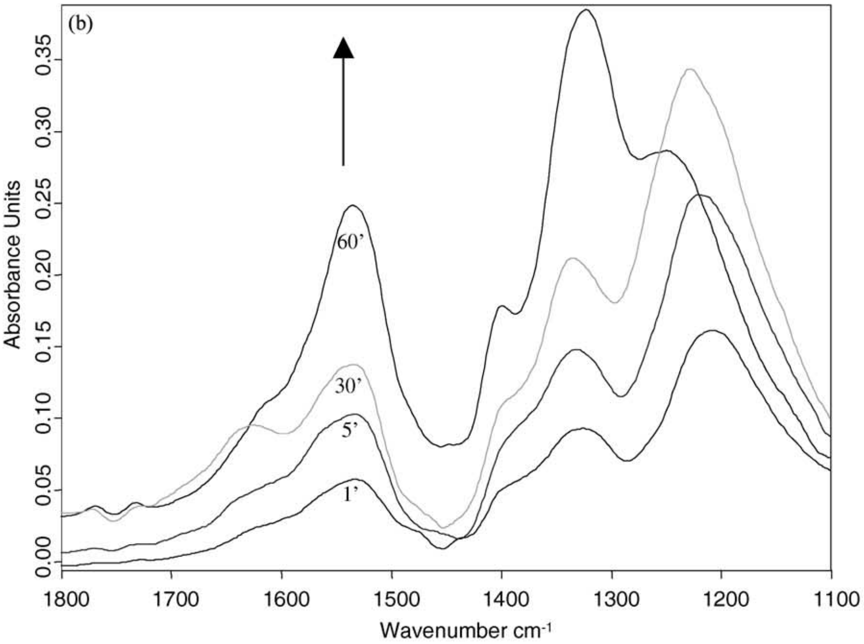
Catalyst	T_{max} (°C)	NO_{max} (%)	$S_{N_2\,max}$ (%)
Pt–CeZr/AlBa	335	39	76
Pt–Ba–Al	354	38	79
Pt–Al_2O_3	223	42	58
Pt–CeZr/Al_2O_3	228	46	63

Reactivity data in the conversion of NO clearly pointed out that the catalytic behaviour of Pt–CeZr/AlBa is very similar to that of Pt–Ba–Al and different from that of Pt supported on alumina or on ceria–zirconia/alumina.

3.3. *DRIFT data*

The behaviour in NO_x storage of Pt–CeZr/AlBa and Pt–Ba–Al samples was monitored also by DRIFT in situ studies. Different type of experiments were made: (i) contact with NO_2 at 100 °C, following the growth of surface species as a function of time-on-stream, (ii) contact with NO in the presence of 5% O_2 at 350 °C, following the growth of surface species as a function of time-on-stream, and (iii) thermodesorption experiments, by contacting NO or NO in the presence of 5% O_2 with the catalyst at 100 °C and then analysing the change of surface species by increasing the reaction temperature in a flow of argon with or without 5% O_2.

In Fig. 4 the comparison is reported of change of surface NO_x species as a function of time in contact with NO_2 at 100 °C for Pt–CeZr/AlBa (Fig. 4a) and



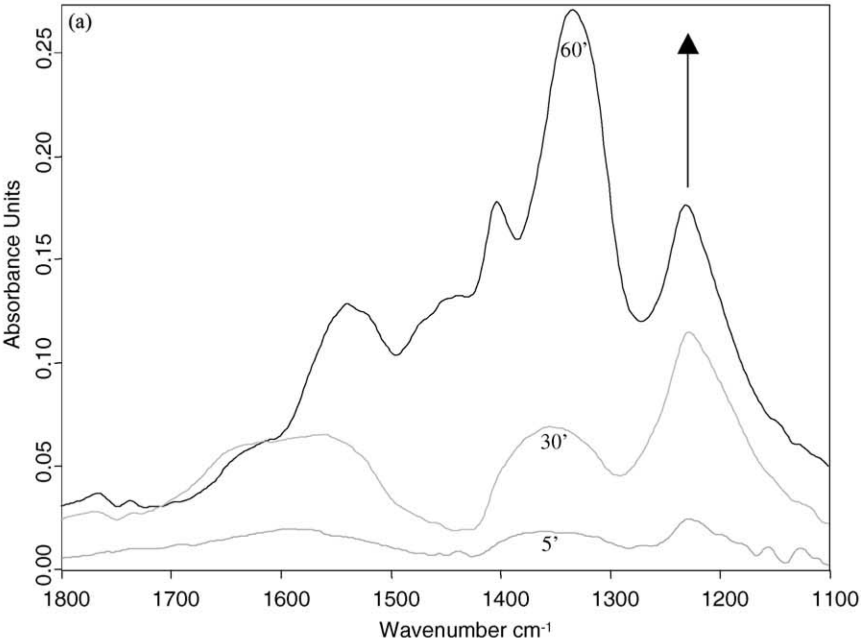


Fig. 4. DRIFT spectra of the change of the NO_x species over Pt–CeZr/AlBa (a) and Pt–Al–Ba (b) as a function of time in contact with NO_2 at 100 °C. Total flow, 100 ml/min; feed composition, 0.1% NO_2, 99.9% Ar.

Pt–Ba–Al (Fig. 4b) samples. Immediately upon contact with NO_2 two broad bands form at about 1210 and 1320 cm^{-1} which rapidly grow in intensity and which may be attributed to the presence of weakly perturbed nitrite anion (ν_{as} and ν_s, respectively) [14]. For longer times in contact with NO_2, the band at 1330 cm^{-1} grow more rapidly than the band at 1210 cm^{-1} and new band at 1400, 1540 and 1630 cm^{-1} become evident. The spectrum is consistent with the presence of nitro and chelating nitro–nitrito species [14] which apparently forms by the conversion of nitrite species. The spectra observed for Pt–CeZr/AlBa and Pt–Ba–Al are very similar as well as their changes as a function of time in contact with NO_2. This suggests that the same type of species form in both cases, namely Ba-nitrite. However, some minor differences could be noted, in particular in the samples after 1 h in contact with NO_2. In fact, in the Pt–Ba–Al the more intense band fall at 1334 cm^{-1} instead of 1324 cm^{-1}, and an additional shoulder is centred at 1445 cm^{-1} (Fig. 4b). This could suggest that a different additional chemisorbed NO_x species form in this catalyst. However, more reasonable interpretation is that the difference is only apparent and caused from the fact that Ba-carbonate species are not displaced in this catalyst by NO_2 chemisorption, differently from Pt–CeZr/AlBa. The displacement of surface Ba-carbonate species caused a negative peak (after subtraction of catalyst background) in the region 1400–1500 cm^{-1} [15] and therefore the apparent differences in the spectrum.

According to this interpretation (supported also by IR evidences of CO_2 detection in the gas phase after NO_2 interaction with Pt–CeZr/AlBa, but not with Pt–Ba–Al), the species which form upon NO_2 chemisorption on the two catalysts are similar, but in Pt–CeZr/AlBa they form by displacement of surface Ba-carbonate species, differently from Pt–Ba–Al. Taking into account that XRD analysis (Fig. 1) indicates that Ba-carbonate is present in the latter sample, but not in the former, it may be concluded that only surface well-dispersed Ba-carbonate may react with NO_2 at r.t. to form Ba-nitrite species, but not bulk-like species detectable by XRD. This indicates that the nature of surface barium species in Pt–CeZr/AlBa is different, at least in part, from those present in Pt–Ba–Al.

Fig. 5 shows the thermodesorption experiments after adsorption of NO at 100 °C in the presence of O_2 and desorption in a hot reactive flow (argon) up to 500 °C. It should be noted that notwithstanding pretreatment in situ at 500 °C (limit of DRIFT cell), the complete desorption of carbonate species does not occurs (see above) and thus a negative peak in the region in the 1400–1500 cm^{-1} overlaps to the positive peak of NO_x chemisorbed species masking the analysis in this spectral region.

Upon adsorption at 100 °C, the spectrum is characterized by a broad band near 1220 cm^{-1} with a shoulder at 1320 cm^{-1} indicating the formation of nitrite ions. Increasing the temperature, these bands disappear and grow into an intense adsorption near 1410 cm^{-1} and a broad and asymmetric band at 1530 cm^{-1}. Although the negative bands of displaced carbonate prevent a clear attribution, the bands are consistent with the formation of mono or bidentate nitrate species. Nitrate adsorbed over ceria or ceria–zirconia give rise to different bands centred at 1630, 1505 and 1305 cm^{-1} [14]. Therefore, IR thermodesorption experiments also confirm the dominant presence of NO_x species chemisorbed over Ba ions in both the samples.

The general features of the spectra of Pt–ZrCe/AlBa (Fig. 5a) and Pt–Ba–Al (Fig. 5b) are similar, but in the latter and intense broad band centred near 1360 cm^{-1} could be detected. This band is observed upon NO interaction with BaO [15] and is thus consistent with the previous indication by XRD that bulk-type BaO crystallites are present on Pt–Ba–Al, while Pt–CeZr/AlBa shows a much better dispersion of Ba, as a consequence of the process of surface migration of Ba from BaO–alumina to the surface of ceria–zirconia overlayer.

A clear peak is also observed near 1740 cm^{-1} which is consistent with NO linearly adsorbed on Pt^{n+} [11] in interaction with alkaline or alkaline-earth ions. The maximum is centred at 1741 cm^{-1} for Pt–CeZr/AlBa and 1736 cm^{-1} for Pt–Ba–Al. NO chemisorbed over $Pt/CeO_2–Al_2O_3$ [16] gives rise to two bands centred at 1810 and 1700 cm^{-1}, the latter is very weak. The frequency of Pt^{n+}–NO species in Pt supported over oxides is reported at 1710 cm^{-1}, while mononitrosyl on metallic Pt at 1785 cm^{-1} [14]. The band at 1740 cm^{-1} (Fig. 5) is thus consistent with a mononitrosyl species on metallic Pt particles with a partially positive charge deriving from near Ba ions. The analogy of the frequency of $Pt^{\delta+}$–NO in Pt–CeZr/AlBa and Pt–Ba–Al

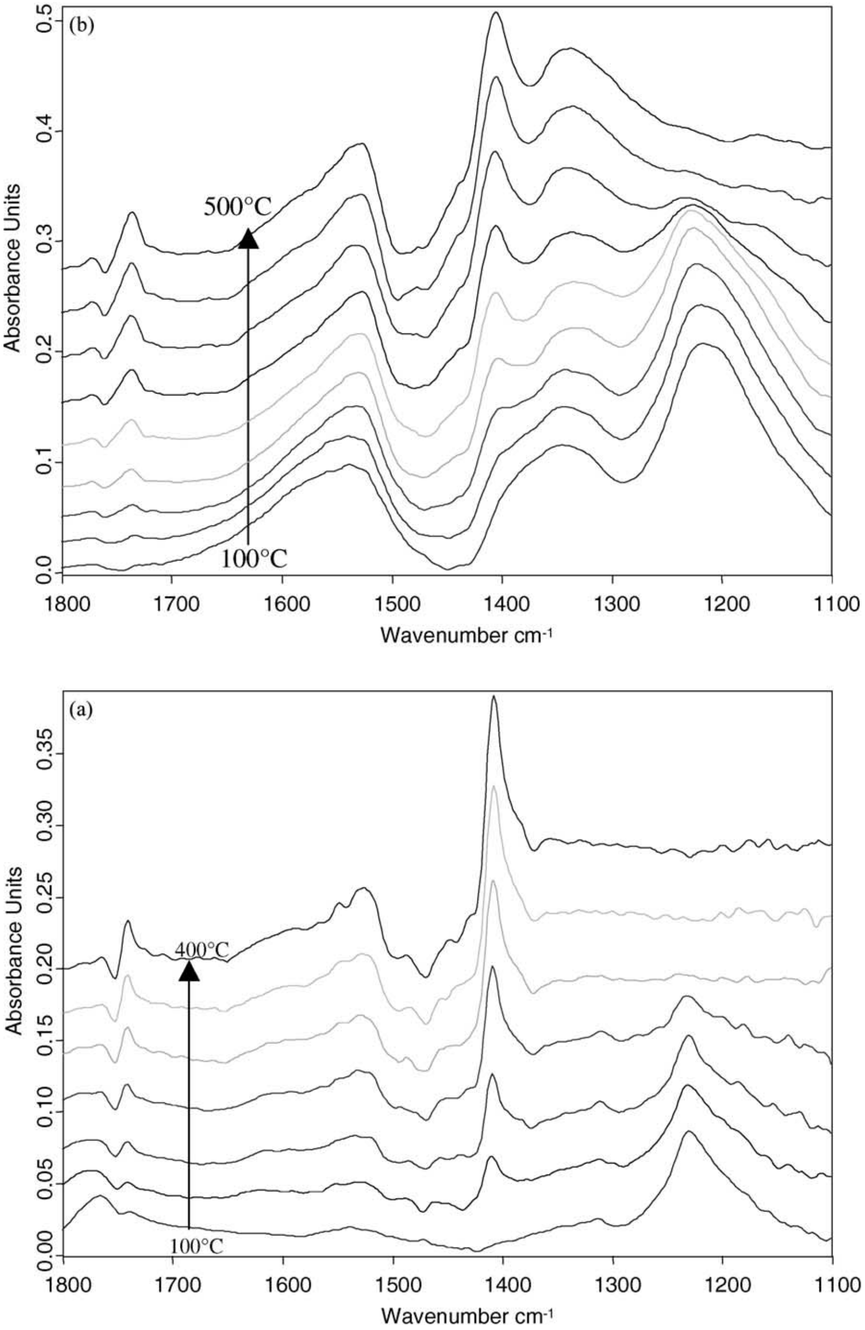


Fig. 5. DRIFT-TPD spectra after NO + O_2 adsorption at 100 °C, over Pt–CeZr/AlBa (a) and Pt–Al–Ba (b). Total flow, 100 ml/min; feed composition, 0.1% NO, 5% O_2, 94.9% Ar. Spectra were collected after 90 min. Temperature ramp from 100 °C until 500 °C (10 °C/min), flow of pure Ar.

indicates the analogy of the Pt particles environment, although the shift to lower frequencies in the latter is consistent with the difference in the nature of Ba species discussed previously.

The results obtained by adsorption of NO and desorption in the presence of O_2 give comparable results and further evidence the presence in Pt–Ba–Al of an additional broad adsorption centred near $1360\,cm^{-1}$, not present in Pt–CeZr/AlBa.

4. Discussion

The original aim of the study was to prepare a thermally stable support which allows improving hydrothermal stability of NO_xSR catalysts. For this reason, alumina was modified according to literature indications [9] by addition of Ba during sol–gel type synthesis in order to improve thermal stability, and a layer of ceria–zirconia was added on this modified alumina, being known the high thermal stability of ceria–zirconia [17] and its positive effect in maintaining a high dispersion of Pt even after severe hydrothermal conditions.

The samples were calcined at high temperature (950 °C) according to the purpose of obtaining thermally stable materials. During this process, however, Ba migrates to surface. Characterisation data (TPR and SEM results) suggest that the surface of alumina is homogeneously covered by ceria–zirconia layer, although further data are necessary to confirm this indication. However, in the hypothesis that ceria–zirconia is covering not homogeneously the alumina surface, leaving thus area of the latter exposed to gas phase reaction, it is expected that during tests in NO reduction by propene and O_2 a bimodal behaviour is observed. In fact, being Pt on alumina or on ceria–zirconia on alumina characterized by a maximum in NO conversion at temperatures about 100 °C lower than those for Pt–BaO on alumina (Table 2), the presence of this species should be revealed during catalytic tests in the reduction of NO. The absence of detection of activity in the conversion of NO in the 200–250 °C temperature range thus indicates that Ba is migrating also over the zirconia–ceria layer.

In situ DRIFT experiments (Figs. 4 and 5) are consistent with this indication and pointed out a comparable behaviour in terms of nature of NO_x species, their thermal stability and kinetic of formation. Data, however, pointed out the probable presence in Pt–Ba–Al of bulk-type BaO particles. Such a species are not present in Pt–CeZr/AlBa, probably due to the mechanism of diffusion as well as to the lower surface concentration of Ba. This is consistent with XRD data (Fig. 1) which indicates the presence of BaO and $BaCO_3$ in Pt–Ba–Al, but not in Pt–CeZr/AlBa.

NO_x storage–reduction tests indicate the good behaviour of Pt–CeZr/AlBa and the comparable results with Pt–Ba–Al (Table 1), although the amount of surface accessible Ba in the latter should be higher. It is worth to note that when Pt–CeZr/AlBa is calcined at about 1100 °C or above, well-evident XRD patterns for $BaAl_{12}O_{19}$ could be evidenced [18]. This suggests that a significant part of Ba is remaining in the bulk of alumina and thus not all Ba migrates to surface. This is consistent with DRIFT data which pointed out that the intensity of spectra of NO_x adsorbed species in Pt–CeZr/AlBa is lower than that of analogous spectra on Pt–Ba–Al. In these DRIFT experiments, the factor determining spectra intensity is the total amount of NO_x storage components, while in NO_xSR catalytic experiments (Table 1 and Fig. 3) due to the high space velocity, the adsorption is essentially dominated by the kinetic of surface adsorption. The fact that the performances of Pt–CeZr/AlBa are comparable to those of Pt–Ba–Al pointed out that due to the better dispersion of Ba ions in Pt–CeZr/AlBa these ions are more reactive that the more aggregated bulk-like BaO species in Pt–Ba–Al. Therefore, the presence of ceria–zirconia layer on alumina, besides to maintain a better dispersion of Pt, probably allows also maintaining a better dispersion of Ba or may play a role in the NO_x storage mechanism.

Although these preliminary data need further studies for a better identification of the nature of surface species and of their reactivity as well as for a more detailed investigation of the performances of Pt–CeZr/AlBa in NO_x storage–reduction and the possibilities for their further promotion, the data demonstrate: (i) the potential relevance of CeZr/AlBa as a novel material to develop advanced NO_xSR catalysts, (ii) the easy diffusion and surface migration of Ba through ceria–zirconia layer, and (iii) the role of this surface migration process as a possibility to control the dispersion of Ba ions and in turn their reactivity. It is known, in fact, that the size of BaO particles have a very relevant role on the NO_xSR catalyst sensitivity to SO_2 poisoning as well as the catalyst regeneration after SO_2 poisoning [2,3]. Furthermore, sintering of BaO particles upon severe hydrothermal treatment occurs, leading to a lowering of the performances. The improvement of these aspects is necessary for the further development of NO_xSR type catalysts. Pt–CeZr/AlBa type catalysts offer new possibilities to achieve these goals.

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