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FULL PAPER



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Effect of water and ammonia on surface species formed during NO_x storage-reduction cycles over Pt-K/Al₂O₃ and Pt-Ba/Al₂O₃ catalysts.

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The effect of water, in the temperature range 25–350 °C, and ammonia at RT on two different surface species formed on Pt-K/Al₂O₃ and Pt-Ba/Al₂O₃ NSR catalysts during NO_x storage-reduction cycles was investigated. The surface species involved are nitrates, formed during the NO_x storage step, and isocyanates, which are seen to be intermediates in N₂ production during reduction by CO. FT-IR experiments demonstrate that the dissociative chemisorption of water and ammonia causes the transformation of the bidentate nitrates and linearly bonded NCO⁻ species into more symmetric species that, reasonably, are adsorbed almost flat on the surface. In the case of water, the effect on nitrates is observable at all the temperature studied; however, the extent of the transformation decreases on increasing temperature, consistently with the decreased extent of dissociatively adsorbed water. It was possible to hypothesize that the dissociative chemisorption of water and ammonia takes place in a competitive way on surface sites able to give bidentate nitrates and linearly bonded NCO⁻ that are dislocated, remaining on the surface as flat species.

Keywords: FT-IR, NSR catalysts, nitrates, isocyanates, water, ammonia

Introduction

The need of developing catalytic systems efficient in the reduction of NO_x under lean conditions is related to the improvement in fuel economy and the reduction in the emissions of CO₂ that require an extensive use of diesel and lean burn gasoline vehicles. Indeed, the Three Way Catalysts (TWCs) used for stoichiometric gasoline engines, are not capable to reduce NO_x under net oxidizing conditions.

For such conditions, the so-called "NO_x storage-reduction catalysts" (NSR) or "Lean NO_x Traps" (LNT) represent a viable solution. The LNT system comprises a long lean phase of about 60 s in which NO_x emitted in the exhaust gases are adsorbed in the form of nitrites and nitrates and a subsequent short rich period of few seconds in which the stored NO_x are reduced by H₂, CO and Hydrocarbons (HC) to produce nitrogen.^{1,2} LNT catalysts are made by a high surface area support (such as γ-Al₂O₃), an alkaline/alkaline-earth metal oxide (such as BaO and/or K₂O) and precious metals (such as Pt).

Several studies were published on the mechanisms of both the NO_x storage^{3–7} and reduction^{8–11} for model LNT catalysts. In previous studies we have analyzed the storage process^{12–17} and the reduction both by H₂^{16, 18–21} and CO^{22–25} over Pt-Ba/Al₂O₃ and Pt-K/Al₂O₃ catalysts by using transient reactivity methods and *in situ* FT-IR spectroscopy. It was found that these catalysts show similar NO_x storage capacity at 350 °C, with initial formation of nitrite species, which are subsequently oxidized into ionic and bidentate nitrates.¹⁶ The ratio between the amount of ionic and bidentate nitrates is higher on Pt-K/Al₂O₃ than on Pt-Ba/Al₂O₃ catalyst. Water vapor, always present in the exhaust gases, has a promoting effect on the storage at low temperature and an inhibiting effect at high temperature.¹²

As for the reduction of stored NO_x by hydrogen, we showed that it occurs through a Pt-catalyzed two-steps in series molecular pathway in which NH₃ is intermediate in N₂ production.^{16, 20}

Water promotes the NO_x reduction by hydrogen.¹⁶

As for the reduction of stored NO_x by CO, it occurs through a Pt-catalyzed surface pathway, like in the case of H₂. It has been observed that under dry conditions isocyanates ad-species are produced by reaction of CO with surface nitrates; these species are involved in the formation of nitrogen upon oxidation by other adsorbed nitrate species, involving, like in the case of H₂, a two-step in series molecular pathway in which NCO⁻ species are intermediates in N₂ production.^{22, 23} In the presence of water, CO reduces nitrates into isocyanates that are readily hydrolyzed to ammonia and CO₂.²⁵

The aim of this work is to study in a systematic way the effect of water and ammonia on surface species present on the two catalysts during the storage-reduction cycles. The surface species considered are nitrates, formed during the NO_x storage step, and isocyanates, which are seen to be intermediates in N₂ production during reduction by CO. The rationalization of the effect of water is of importance being water always present in the feed during actual operating conditions. Along similar lines, it is of interest to study the effect of NH₃ since this species is intermediate in N₂ formation during reduction with hydrogen. We have already reported some observations about these effects in previous works^{16, 26}; however, the present research allows us to find out a common thread that bounds the behavior of the different surface species upon interaction with these two molecules. Moreover, it allows to investigate more deeply the nature of NCO⁻ species present at the catalyst surfaces and to propose an alternative assignment of their spectroscopic features with respect to that generally accepted.^{11, 27}

This work follows on from papers already published by other authors about FT-IR study of the water effect on nitrates species for these systems. In particular, Szanyi et al.^{28, 29} and Kim et al.³⁰ reported about water-induced morphology changes in BaO/γ-Al₂O₃ materials at room temperature. The results of their study reveal that in the presence of water surface Ba-nitrates convert to

bulk nitrates and water facilitates the formation of large Ba(NO₃)₂ particles.

Toops et al.^{6, 31} reported DRIFTS spectra in which effect of water on surface nitrate distribution in different species for a Pt-K/Al₂O₃ catalyst is well evident. However, they did not discuss about this aspect since they were mainly interested in elucidating the key steps in the absorption of NO_x and to study the variation in the adsorption capacity in presence of water and CO₂.

Experimental

Pt-K/Al₂O₃ (1/5.4/100 w/w) and Pt-Ba/Al₂O₃ (1/20/100 w/w) catalysts, with equal molar amounts of the storage component (0.146 mol K/ or Ba/ 100g Al₂O₃) were prepared by incipient wetness impregnation of γ -alumina (Versal 250 from UOP, surface area 200 m²/g) with aqueous solutions of dinitro-diammine platinum (Strem Chemicals, 5% Pt in ammonium hydroxide), so as to yield 1wt.% Pt loading, followed by a solution of potassium acetate or barium acetate (Aldrich, 99%). After each impregnation step, the powders were dried overnight in air at 80 °C and calcined at 500 °C for 5 h. The molar amounts of storage components were chosen on the base of a calculation for the formation of K₂O or BaO mono-layers. As a matter of fact, as already demonstrated in our previous works^{17, 32}, no hydroxyls typical of alumina were detected on the activated samples and CO admission at RT on freshly reduced samples followed by FT-IR spectroscopy showed no bands due to CO adsorbed onto Al³⁺ Lewis acid sites, in agreement with the high coverage of the alumina support by the storage phases.

Absorption/transmission IR spectra have been obtained on a Perkin-Elmer FT-IR System 2000 spectrophotometer equipped with a Hg-Cd-Te cryo-detector, working in the range of wavenumbers 7200-580 cm⁻¹ at a resolution of 2 cm⁻¹ (number of scans ~20). For IR analysis powder catalyst has been compressed in self-supporting disc (of about 10 mg cm⁻²) and placed in a commercial heatable stainless steel cell (Aabspec) allowing thermal treatments *in situ* under vacuum or controlled atmosphere up to 600 °C. Pellets have been activated by some storage-reduction cycles at 350 °C in NO₂ and H₂. This activation stage was necessary to convert a large part of barium and potassium carbonate phase present on the catalyst after the calcination into the oxide phase. For Pt-K/Al₂O₃ only one storage-reduction cycle is needed to remove large part of carbonates from the surface¹⁷, while Pt-Ba/Al₂O₃ system required three or four cycles to convert a large part of the very stable barium carbonate phase.¹³ Afterward the catalyst was outgassed and oxidized in dry oxygen at 500 °C (activated sample), and cooled in oxygen down to RT and spectra were run at increasing temperature from RT up to 350 °C.

NO_x storage was performed by admitting freshly prepared NO/O₂ mixture (P_{NO} = 5 mbar; P_{O₂} = 20 mbar) at 350 °C. After the storage phase the catalysts were evacuated at 350 °C and cooled down to room temperature (RT). Alternatively, after a storage phase the catalysts were evacuated at 350 °C and reduced with CO (P_{CO} = 10 mbar) at 350 °C in order to form NCO⁻ species^{22, 23} and cooled down to room temperature (RT). The interaction of H₂O and NH₃ with nitrates and NCO⁻ surface species has been then carried out at increasing gas pressure up to 5 mbar at RT. In the case of water the interaction was also studied at increasing

temperature up to 350 °C.

In the figures, the spectra recorded during the interaction with a gas are reported as difference spectra: the spectrum subtracted is always that recorded at the same temperature after the activation treatment.

XRD analyses were performed on a PW 3050/60 X'Pert PRO MPD diffractometer from PANalytical using the Cu K_{α1} radiation (λ = 1.5406 Å) in step mode between 5 and 80° 2θ with a step of 0.02%.

Results and discussion

Detailed textural, structural and morphological characterization of the two catalysts has been already reported in our previous papers.^{17, 32} Here, we only recall some useful information: the surface areas and pore volumes measured by N₂ adsorption-desorption at -196 °C are 176 m²/g and 0.9 cm³/g for the Pt-K/Al₂O₃ sample and 137 m²/g and 0.81 cm³/g for the Pt-Ba/Al₂O₃ sample. Also the storage properties characterized by *in situ* FT-IR spectroscopy at different temperature have been already reported in our previous paper^{13, 16, 33} and here we only report in Table 1 some useful information about the band frequencies of the different nitrate species formed at the surface of the two systems at the end of the storage step performed at 350 °C (Figures 1 and 2, curves a). As already recalled in the introduction, the storage in presence of NO/O₂ occurs with the initial formation of nitrite species, which are subsequently oxidised to nitrates. Accordingly only nitrates are present at the end of the storage. Notably, due to the good spread of the basic phases, no nitrates characteristic of the alumina phase are detected. Indeed, two different types of nitrates are mainly formed, both on the basic phase, i.e. bidentate

Table 1 Nitrate species and related IR bands formed upon adsorption of NO/O₂ at 350 °C on Pt-K/Al₂O₃ and Pt-Ba/Al₂O₃ catalysts.

Catalyst	Nitrates species	Band positions (cm ⁻¹)	Assignments
Pt-K/Al ₂ O ₃	bidentate nitrates	1620-1500 1315 1020-1000	v(N=O) v _{asym} (NO ₂) v _{sym} (NO ₂)
	ionic nitrates	1390, 1365-70 1040	v _{asym} (NO ₃) v _{sym} (NO ₃)
Pt-Ba/Al ₂ O ₃	bidentate nitrates	1620-1500 n.d. 1032	v(N=O) v _{asym} (NO ₂) v _{sym} (NO ₂)
	ionic nitrates	1460-1400, 1360-1300 1040	v _{asym} (NO ₃) v _{sym} (NO ₃)

n.d. = band not detectable because superimposed to other bands.

nitrates and a highly symmetric species that we named ionic nitrates. However, it is important to underline that both the nitrate types show an interaction with the basic surface mainly of ionic character. Nevertheless, we use the name "ionic nitrates" for defining a species that, on the basis of the spectroscopic features, can be thought with a nearly flat geometry on the surface, i.e. a species with symmetry similar to that found in the nitrate salts.

It is worth of note that the total amounts of NO_x stored at the end of the adsorption step are very similar on the two catalysts and

correspond to a fraction of K and Ba sites involved in the NO_x storage close to 40% and 20%, respectively.³⁴ Nitrates are formed on the most reactive sites, which are the most coordinatively unsaturated sites. As a consequence, at the end of the storage, a large part of the surface sites are free from nitrates.

Water and ammonia effect on nitrates

The interaction of water at RT with the nitrates formed at 350 °C in presence of NO/O_2 is shown in Figures 1 and 2 for Pt-K/ Al_2O_3 and Pt-Ba/ Al_2O_3 , respectively. Solid curves "a" are spectra recorded at RT after NO_x storage and evacuation at 350 °C. Upon H_2O admission at increasing pressure from 0.01 mbar up to 5 mbar (solid curves b-e) the bands of bidentate nitrates (at 1545, 1315 and 1007 cm^{-1} for Pt-K/ Al_2O_3 ; at 1555 and 1032 cm^{-1} for Pt-Ba/ Al_2O_3) are gradually eroded and those of ionic nitrates (at 1390, 1365 and 1040 cm^{-1} for Pt-K/ Al_2O_3 ; at 1425-1410, 1325-1345 and 1040 cm^{-1} for Pt-Ba/ Al_2O_3) increase in intensity.

For both catalysts the consumption of bands related to bidentate nitrates is complete at water pressure well lower than 5 mbar (Figures 1A and 2, curves d, 0.7 and 0.3 mbar, respectively). Increasing the water pressure up to 5 mbar (curves e) no changes are observed for nitrate bands over Pt-K/ Al_2O_3 catalyst. Conversely, for Pt-Ba/ Al_2O_3 the maximum intensity of the bands related to ionic nitrates sensibly increases and contemporary these bands shift from 1425 to 1410 cm^{-1} and from 1325 to 1345 cm^{-1} . It is worth of note that the increased intensity is associated to a sharpening of the two bands. In fact, their integrated intensities passing from curve "d" to curve "e" in Figure 2 are unchanged, according with the fact that they are related to the same amount of ionic nitrates.

On both catalysts, the absorption related to the bending mode of molecular adsorbed water is observed starting from 0.02-0.04 mbar (Figures 1 and 2, curves c) at about 1630-1640 cm^{-1} . The associated stretching modes are responsible for the broad band centered at 3300 cm^{-1} (reported in Figure 1B for Pt-K/ Al_2O_3 , not reported for Pt-Ba/ Al_2O_3 for sake of brevity). At water pressure lower than 0.02-0.04 mbar (Figure 1B, curve b), before the increase of molecular H_2O bands, the increase of the band at 3535 cm^{-1} related to the stretching mode of surface hydroxyls is observed. Moreover, the very broad band extending from 1200 until wavenumbers lower than 1000 cm^{-1} is related to the bending modes of surface hydroxyls.³⁵

The prolonged outgassing at RT (dotted curves in Figures 1 and 2) causes the complete desorption of molecular water (erosion of the bands at 1630-1640 and 3300 cm^{-1}), but no significant changes in the nitrate region for Pt-K/ Al_2O_3 catalyst. For Pt-Ba/ Al_2O_3 sample the desorption of molecular water causes the comeback of the two bands related to ionic nitrates towards the positions and linear intensities showed in spectrum "d" of Figure 2. This behavior can be reasonably explained taking into account

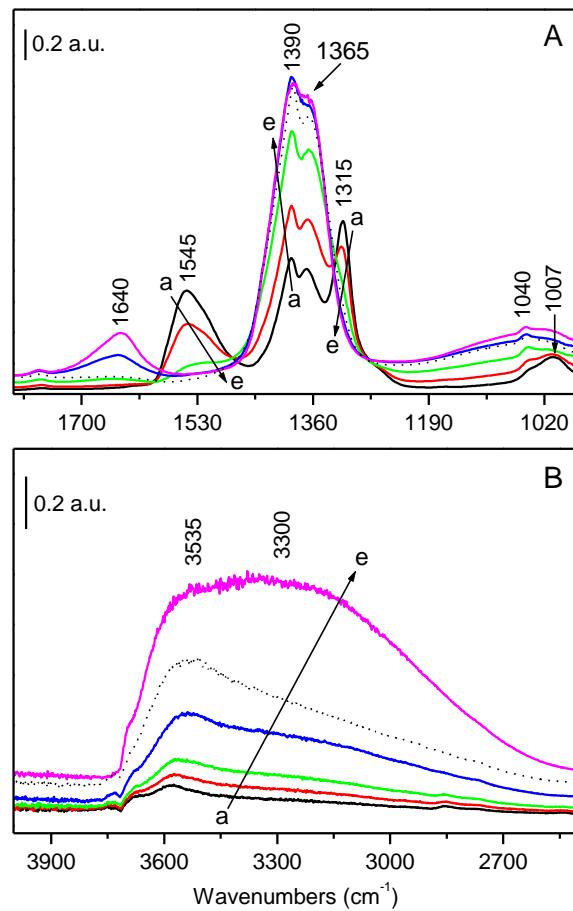


Fig. 1 Interaction of H_2O at RT with nitrates previously stored at 350 °C over Pt-K/ Al_2O_3 catalyst. (A) nitrate stretching region and (B) O-H stretching region. Solid curve a: spectrum of nitrates stored by NO/O_2 at 350 °C, evacuated at 350 °C and cooled down to RT. Solid curves b-e: admission of H_2O at 0.01 mbar (curve b), 0.04 mbar (curve c), 0.7 mbar (curve d) and 5 mbar (curve e). Dotted curve: evacuation at RT after water admission.

that the two bands arise from the splitting of the double degenerate $\nu_{\text{asym}}(\text{NO}_3)$ mode of free nitrate ion, whose symmetry is quite lowered in the flat adsorbed species. Consequently, the decrease in the separation of the two bands in presence of high amounts of molecular water (spectrum "e" of Figure 2) can be related to a marked increase in the symmetry of the surface ionic nitrates due to the formation of a liquid-like water layer. This phenomenon is not observed for the ionic nitrates on the Pt-K/ Al_2O_3 catalyst: as a matter of fact, the ionic nitrate bands over Pt-K/ Al_2O_3 are particularly sharp and much less separated than those observed over Pt-Ba/ Al_2O_3 catalyst. This indicates higher symmetry of the ionic species on the former system. As a consequence, ionic nitrates on Pt-K/ Al_2O_3 catalyst are not sensibly influenced by the presence of physisorbed water.

For both catalysts, outgassing at increasing temperature (not reported) causes the decrease of bands related to stretching (at 3535 cm^{-1}) and bending modes (at frequencies lower than 1200 cm^{-1}) of surface hydroxyls. Contemporary, the decrease of ionic nitrate peaks and the reappearance of those of bidentate ones are observed in the temperature range 100-250 °C. At temperature higher than 250 °C both ionic and bidentate nitrate bands

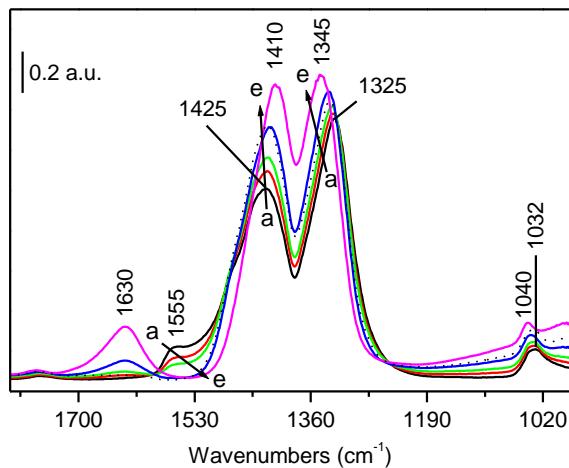


Fig. 2 Interaction of H_2O at RT with nitrates previously stored at $350\text{ }^\circ\text{C}$ over the Pt-Ba/Al₂O₃ catalyst. Solid curve a: spectrum of nitrates stored by NO/O₂ at $350\text{ }^\circ\text{C}$, evacuated at $350\text{ }^\circ\text{C}$ and cooled down to RT. Solid curves b-e: admission of H_2O at 0.01 mbar (curve b), 0.02 mbar (curve c), 0.3 mbar (curve d) and 5 mbar (curve e). Dotted curve: evacuation at RT after water admission.

decrease. Reasonably, in the temperature range $100\text{--}250\text{ }^\circ\text{C}$ the surface de-hydroxylation causes the re-conversion of ionic nitrates into bidentate ones. At temperature higher than $250\text{ }^\circ\text{C}$ bidentate nitrates decompose. Taking into account that, after NO/O₂ admission, the catalysts were outgassed at $350\text{ }^\circ\text{C}$, this means that bidentate nitrates re-formed after water adsorption-desorption cycle show a thermal stability lower than that of bidentate nitrates initially formed upon NO/O₂ admission.

The experiments clearly demonstrate that the dissociative adsorption of water leading to OH groups, and not the presence of molecularly adsorbed water, causes the transformation of the bidentate nitrates into the ionic ones. This is also confirmed by the fact that the transformation is observable for water interaction at higher temperature up to $350\text{ }^\circ\text{C}$. Indeed, at temperature in the range $150\text{--}350\text{ }^\circ\text{C}$ the interaction with water leads to surface hydroxylation only and not to adsorbed molecular water. As expected, the transformation extent decreases on increasing temperature in relation to the decreased surface hydroxylation. In Figure 3 the spectrum obtained during the interaction of water (5 mbar) at $350\text{ }^\circ\text{C}$ (curves a) with nitrates previously stored at $350\text{ }^\circ\text{C}$ over the Pt-K/Al₂O₃ catalyst is compared with the spectrum obtained after water interaction at RT and subsequent outgassing at RT (curves b). The spectrum at RT is reported after outgassing in order to remove molecularly adsorbed water. It is possible to observe that, differently from the case at RT, at $350\text{ }^\circ\text{C}$ the transformation of bidentate nitrates into ionic ones is not complete (Figure 3A). As expected, this is due to a lower surface hydroxylation with respect to that observed at RT (Figure 3B). Actually, at high temperature the dissociative adsorption of water still happens, but the stability of hydroxyls is lower than at RT.

It is worth of note that at $350\text{ }^\circ\text{C}$ the split of the $\nu_{\text{O-N-Oasym}}$ mode at 1390 and 1365 cm^{-1} of ionic nitrates is lost (see curve a in Figure 3A), showing an increase in the symmetry of this adsorbed species. This is reasonable, because an increase of thermal energy increases the mobility of the surface species and, as a consequence, the average surrounding of each oxygen atom in

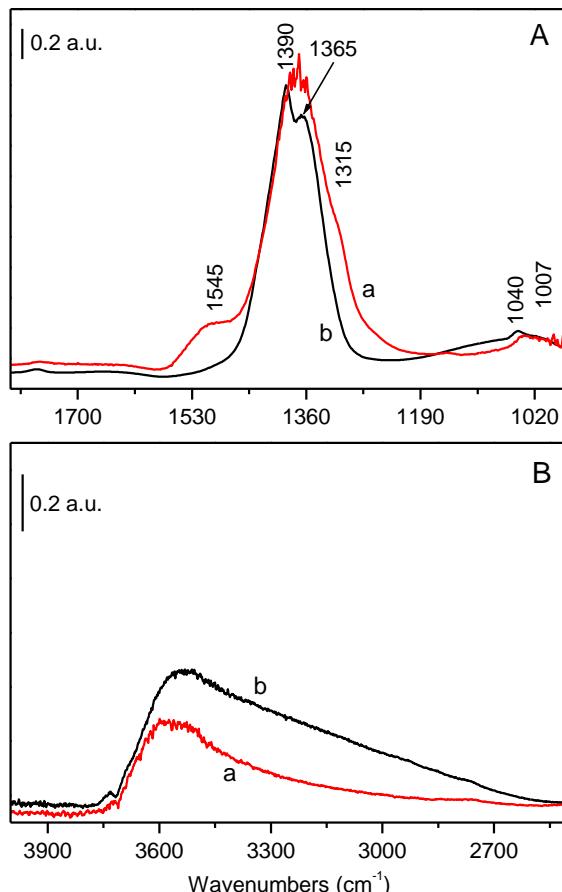


Fig. 3 Comparison between the spectrum obtained during the interaction of water (5 mbar) at $350\text{ }^\circ\text{C}$ with nitrates previously stored at $350\text{ }^\circ\text{C}$ over the Pt-K/Al₂O₃ catalyst with H_2O (5 mbar) at $350\text{ }^\circ\text{C}$ (curves a) and after water interaction at RT and subsequent outgassing at RT (curves b). (A) nitrate stretching region and (B) O-H stretching region.

NO_3^- is similar.

As already mentioned in the introduction, Szanyi et al.^{28, 29} and Kim et al.³⁰ reported about water-induced morphology changes in BaO/ γ -Al₂O₃ materials at room temperature. In particular, their studies revealed that in the presence of water surface Ba-nitrates convert to bulk nitrates and water facilitates the formation of large Ba(NO₃)₂ particles, as pointed out by XRD measurements performed both by X-ray diffractometer³⁰ and synchrotron light source,^{28, 29} which allows time-resolved XRD study. From our XRD analyses, no peaks related to KNO₃ or Ba(NO₃)₂ were observed on our samples before and after water interaction at RT with surface nitrates stored by NO/O₂ mixture at $350\text{ }^\circ\text{C}$. Only alumina diffraction peaks can be observed as reported in our previous works for activated samples.^{17, 32} So, we exclude the formation of bulk nitrates on our catalysts and we are confident to consider as surface species all the nitrates observed by FT-IR measurements.

As already reported elsewhere by some of us for Pt-K/Al₂O₃,¹⁶ the effect of water dissociation allows the evaluation of the ratio between the amounts of bidentate and ionic nitrates at the end of the storage. The same evaluation is more difficult for Pt-Ba/Al₂O₃ due to the very low amount of bidentate nitrates at the end of the storage. For Pt-K/Al₂O₃ the integrated intensities of the bands

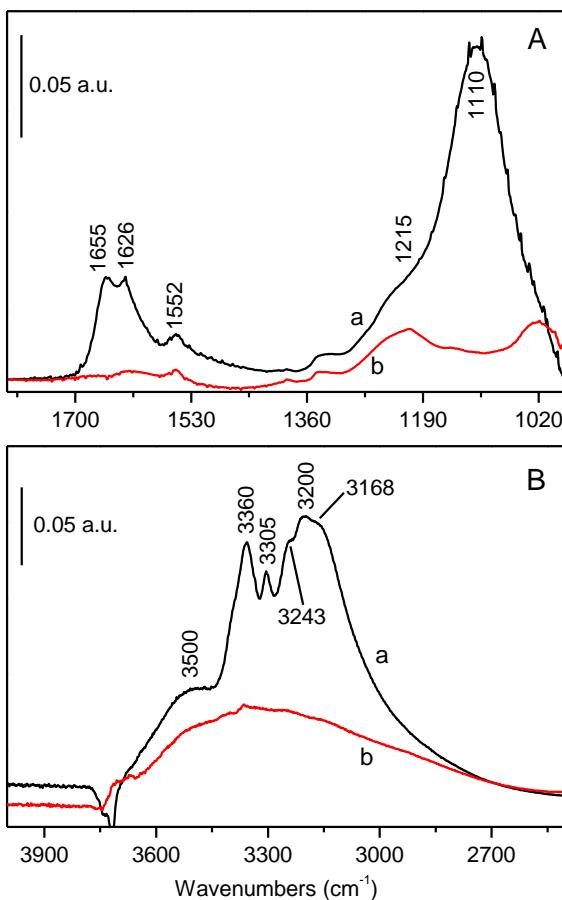


Fig. 4 Adsorption of NH_3 (5 mbar) at RT on Pt-K/Al₂O₃ catalyst before the NO_x storage (curve a). Curve b: after evacuation at RT.

related to ionic nitrates before and after H₂O interaction ($I_{\text{ion.}}$ and $I_{\text{ion. H}_2\text{O}}$, respectively) can be coarsely estimated. The ratio $I_{\text{ion. H}_2\text{O}}/I_{\text{ion.}}$ is about 2. Taking into account that all bidentate nitrates are transformed into ionic ones by water interaction, the value of the ratio $I_{\text{ion. H}_2\text{O}}/I_{\text{ion.}}$ shows that the amounts of bidentate and ionic nitrates present on the surface before the water admission are comparable.

The effect of ammonia is now considered. For sake of clarity, in the following discussion we consider Pt-K/Al₂O₃ catalyst only, being all the observations made true also for the Pt-Ba/Al₂O₃ system. First of all, NH_3 (5 mbar) was adsorbed at RT before the NO_x storage (Figure 4, curve a): bands assignable to the modes of adsorbed NH_3 polarized on the K⁺ ions or bonded to the surface hydroxyls are observed. In particular, the absorptions at 1655 and 1626 cm^{-1} are assigned to the δ_{asym} modes, the shoulder at 1215 cm^{-1} and the band at 1110 cm^{-1} to the δ_{sym} modes. Bands at 3360 and 3305 cm^{-1} are assigned to ν_{asym} modes and that at 3243, 3200 and 3168 cm^{-1} to ν_{sym} modes. All the stretching modes of adsorbed ammonia are superimposed to stretching modes of hydrogen bonded hydroxyls (shoulder at 3500 cm^{-1}). The spectral region of the NH stretching vibrations is relatively complex due to the following: (i) loss of the degeneracy of the double degenerate ν_{asym} mode of free ammonia, as a consequence of the adsorption; (ii) heterogeneity of surface sites that bonded ammonia; (iii) presence of bands related to coupling between the

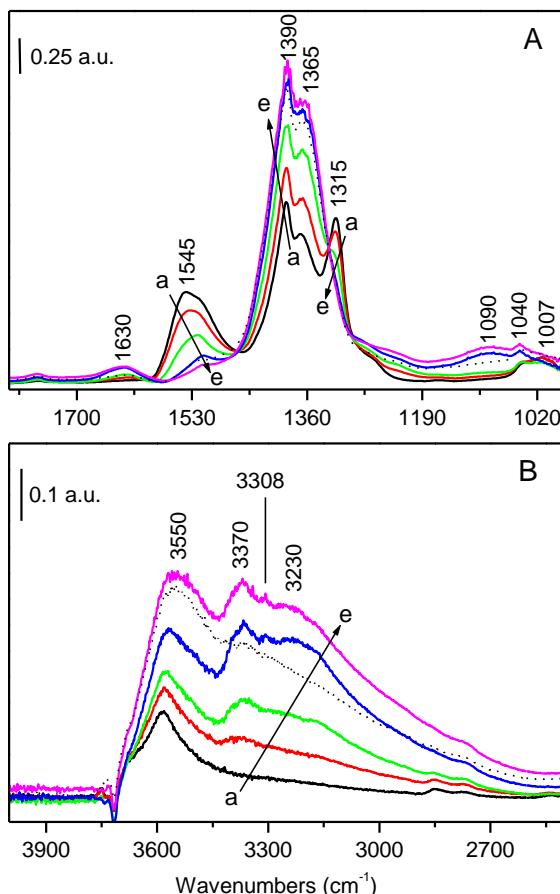


Fig. 5 Interaction of NH_3 at RT with nitrates previously stored at 350 °C over the Pt-K/Al₂O₃ catalyst. (A) nitrate stretching region and (B) O-H and N-H stretching region. Solid curve a: spectra of nitrates stored by NO/O₂ at 350 °C, evacuated at 350 °C and cooled down to RT. Solid curves b-d: admission of NH_3 at 0.04 mbar (curve b), 0.4 mbar (curve c) and 5 mbar (curve d). Curve e: interaction with 5 mbar of NH_3 for 1h. Dotted curve: evacuation at RT after ammonia admission.

ν_{sym} mode and the first overtone of δ_{asym} mode. Points (i) and (ii) can also account for the presence of two bands related to the δ_{asym} mode of the adsorbed molecule at 1655 and 1626 cm^{-1} .

It is worth of note the peak at 1552 cm^{-1} , assignable to the bending mode of NH_2^- surface species formed by dissociative chemisorption of NH_3 over strongly basic O²⁻ sites. After outgassing at RT (Figure 4, curve b) the bands related to molecular adsorbed NH_3 are drastically reduced, while the decrease of the absorption at 1552 cm^{-1} related to NH_2^- is definitely less marked. The very broad band in the region 3600-2800 cm^{-1} still present after outgassing at RT is related to hydroxyl groups formed by the dissociative chemisorption of NH_3 and to pre-existing hydroxyls perturbed by the bond with residual molecular ammonia.

The interaction of ammonia at RT with the nitrates formed at 350 °C with NO/O₂ is shown in Figure 5 for Pt-K/Al₂O₃. Solid curve "a" is the spectrum recorded at RT after NO_x storage and evacuation at 350 °C. Upon NH_3 admission at increasing pressure from 0.04 mbar up to 5 mbar (solid curves b-d) in the 1700-1000 cm^{-1} spectral region (section A) a strong decrease of bidentate nitrate bands and a noticeable increase of those of ionic ones is

observed simultaneously with an intensification and loss in resolution of the $\delta_{\text{asym}}(\text{NH}_3)$ modes (only one broad peak is now present at 1630 cm^{-1}), a decrease in intensity of the $\delta_{\text{sym}}(\text{NH}_3)$ mode at 1090 cm^{-1} , and a decrease in the resolution of the $\nu_{\text{asym}}(\text{NH}_3)$ and $\nu_{\text{sym}}(\text{NH}_3)$ modes of adsorbed ammonia. Notably, the adsorption of ammonia strongly perturbs the stored nitrates, in a way very similar to the perturbation produced by water, i.e. transforming bidentate nitrates into ionic ones. However, the transformation is slower than that observed for water. As a matter of fact, curve "d" in Figure 5A is obtained immediately after the admission of 5 mbar of ammonia, curve "e" after 1h of interaction with 5 mbar of ammonia: the erosion of band at 1545 cm^{-1} related to bidentate nitrates continues after 1h and it is not complete. Contemporary, the bands at 1630 , 3370 , 3308 and 3230 cm^{-1} related to molecular adsorbed NH_3 does not change with time, while the absorptions in the region 3700 - 2700 cm^{-1} (Figure 5B) increases in parallel with the ammonia dissociation on the surface, forming OH^- groups. At variance, as seen in the case of water the erosion of bidentate nitrates is immediately complete even with pressure lower than 1 mbar and it does not show time dependence.

The prolonged outgassing at RT (dotted curves in Figure 5) causes the almost complete desorption of molecular adsorbed ammonia, but no significant changes in the nitrate region. As in the case of water, the experiments clearly demonstrate that the dissociative chemisorption of ammonia and not molecular adsorbed ammonia causes the transformation of the bidentate nitrates into the ionic ones, even if it is also clear that in the presence of the stored NO_x the vibration modes of adsorbed NH_3 are modified. It is also evident that the dissociative chemisorption of ammonia (leading to the formation of hydroxyls and NH_2^- groups), responsible for nitrate transformation, is slower than the water dissociation.

Water and ammonia effect on NCO^- species

The attention is now focused on Pt-Ba/ Al_2O_3 and Pt-K/ Al_2O_3 catalysts submitted to NO_x storage and reduction with CO at 350°C , exhibiting NCO^- species, as already discussed elsewhere by some of us.^{22, 23} Bands related to $\nu_{\text{asym}}(\text{NCO})$ are present at 2230 and 2168 cm^{-1} for Pt-Ba/ Al_2O_3 (Figure 6A, curve a) and at 2223 and 2164 cm^{-1} for Pt-K/ Al_2O_3 (Figure 7A, curve a).

In the literature, the higher frequency component of the $\nu_{\text{asym}}(\text{NCO})$ doublet over Pt-Ba/ Al_2O_3 systems is generally assigned to NCO^- species adsorbed on Al^{3+} sites in tetrahedral coordination, while the lower frequency component to NCO^- species on Ba^{2+} sites.^{11, 27} This assignment does not match with our results, reported elsewhere³², evidencing an almost complete coverage of the alumina support by the barium phase and thus the unavailability of Al^{3+} sites. The same can be affirmed for Pt-K/ Al_2O_3 .¹⁷ We thus ascribe the two components to $\nu_{\text{asym}}(\text{NCO})$ modes of two species adsorbed over different Ba (or K) sites. The proposal is further supported by the behavior of NCO^- species upon water admission. Indeed, as in the case of nitrates, upon water admission at increasing pressure from 0.01 - 0.04 mbar up to 5 mbar the band at $2230/2223 \text{ cm}^{-1}$ is gradually eroded and the band at $2168/2164 \text{ cm}^{-1}$ increases in intensity (Figures 6A and 7A). Note that, as in the case of nitrates, this transformation involves species with high thermal stability.³⁶

The prolonged outgassing at RT (Figure 6A, dotted curve, and

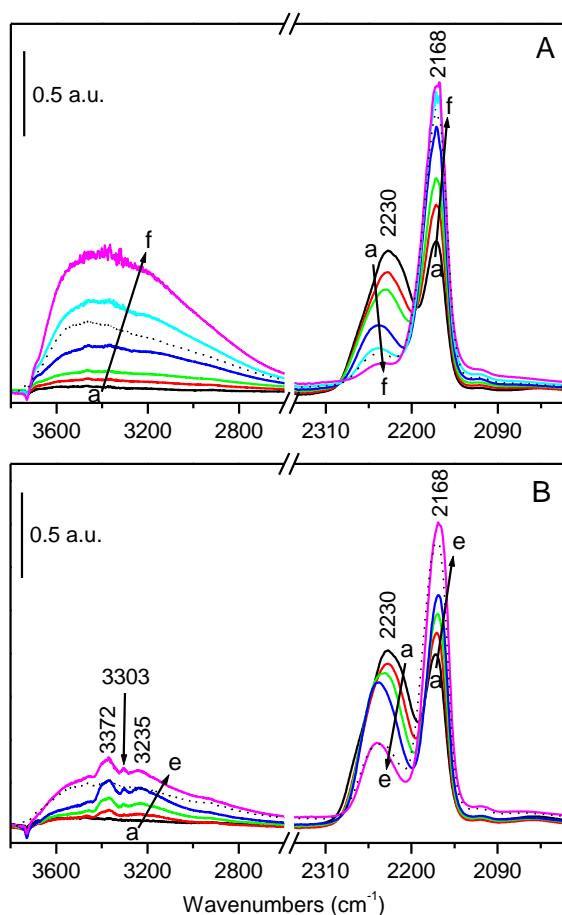


Fig. 6 Section A: interaction of H_2O at RT with NCO^- species previously formed over the Pt-Ba/ Al_2O_3 catalyst. Solid curve a: spectrum of NCO^- species previously formed by NO_x reduction with CO at 350°C , evacuated at 350°C and cooled down to RT. Solid curves b-f: admission of H_2O at 0.04 mbar (curve b), 0.08 mbar (curve c), 0.2 mbar (curve d), 0.5 mbar (curve e) and 5 mbar (curve f). Dotted curve: evacuation at RT after water admission. Section B: interaction of NH_3 at RT with NCO^- species previously formed over the Pt-Ba/ Al_2O_3 catalyst. Solid curve a: spectrum of NCO^- species previously formed by NO_x reduction with CO at 350°C , evacuated at 350°C and cooled down to RT. Solid curves b-d: admission of NH_3 at 0.03 mbar (curve b), 0.6 mbar (curve c) and 5 mbar (curve d). Solid curve e: interaction with 5 mbar of NH_3 for 2h. Dotted curve: evacuation at RT after ammonia admission.

Figure 7B, curve a) causes the complete desorption of molecular water; contemporary, only small amount of NCO^- species related to the lower frequency component is re-converted into the higher frequency one. For both the catalysts, outgassing at increasing temperature (Figure 7B for Pt-K/ Al_2O_3 catalyst, not reported for Pt-Ba/ Al_2O_3 for sake of brevity) provokes the decrease of the NCO^- species related to lower frequency band and the increase of those related to the higher frequency band simultaneously with surface de-hydroxylation up to 200°C . At temperature higher than 200°C the two NCO^- species start to decompose due to the occurrence of hydrolysis reaction.

Water interaction with isocyanates at 350°C was also tested (not reported in figure): immediately after water admission the effect is the same observed at RT (less marked due to the lower degree of hydroxylation), then hydrolysis of NCO^- into NH_3 and CO_2 occurs.

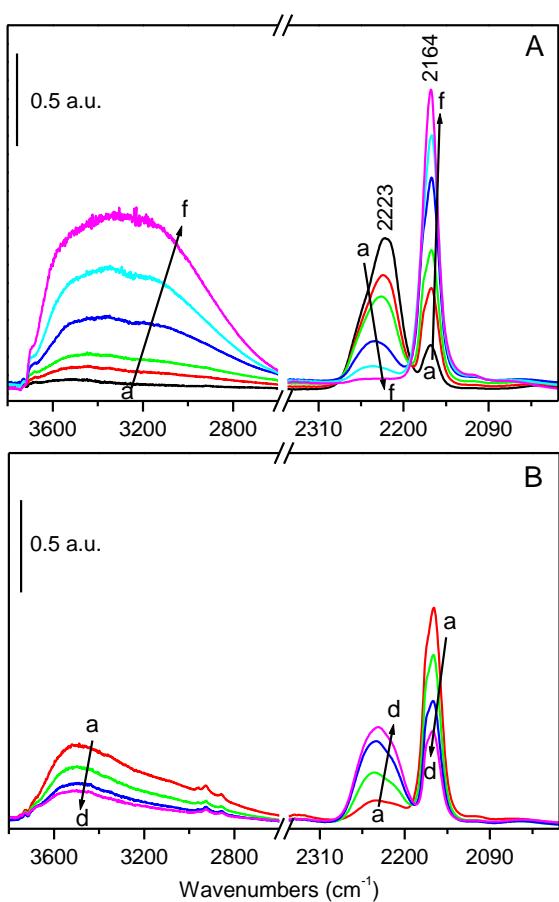


Fig. 7 Section A: interaction of H_2O at RT with NCO^- species previously formed over the Pt-K/Al₂O₃ catalyst. Curve a: spectrum of NCO^- species previously formed by NO_x reduction with CO at 350 °C, evacuated at 350 °C and cooled down to RT. Curves b-f: admission of H_2O at 0.01 mbar (curve b), 0.02 mbar (curve c), 0.07 mbar (curve d), 0.6 mbar (curve e) and 5 mbar (curve f). Section B: subsequent evacuation at RT (curve a), 100 °C (curve b), 150 °C (curve c) and 200 °C (curve d).

On the basis of these results, the first hypothesis was that the species related to 2168/2164 cm⁻¹ band could be a hydrogen-containing species. To check this possibility, the reactivity of NCO^- species toward D₂O over Pt-Ba/Al₂O₃ catalyst was studied: in the case of H-containing species, a red-shift of the 2168 cm⁻¹ band would be observed. Actually, using D₂O, again the transformation of the 2230 cm⁻¹ band into the 2168 cm⁻¹ one is observed, but no changes in the band positions are evidenced. This excludes the presence of hydrogenated species. As a consequence, following from the results obtained with nitrates, we suggest for both catalysts the presence of two NCO^- species both adsorbed on Ba or K phase, being the band at 2230/2223 cm⁻¹ related to NCO^- linearly N-bonded on surface sites and the band at 2168/2164 cm⁻¹ related to NCO^- species flat on the surface. We refer to the NCO^- species with a flat geometry on the surface as "ionic isocyanates", in order to define a species very similar to that found in the inorganic salts. This hypothesis can be also supported by the fact that 2230/2223 cm⁻¹ are wavenumbers characteristic of isocyanates in organic compounds (N-bonded species), while 2168/2164 cm⁻¹ are wavenumbers found for cyanate ion in inorganic salts.^{37, 38}

As reported for nitrates, the effect of water dissociation allows the evaluation of the ratio between the amounts of linear and ionic isocyanates at the end of storage and reduction performed with CO. The integrated intensities of the bands related to ionic isocyanates before and after H_2O interaction (I_{ion} and $I_{\text{ion}}^{\text{H}_2\text{O}}$, respectively) can be coarsely estimated for both the catalysts. The ratio $I_{\text{ion}}^{\text{H}_2\text{O}} / I_{\text{ion}}$ is about 5 for Pt-K/Al₂O₃. Since all linear isocyanates are transformed into ionic ones by water interaction on the Pt-K/Al₂O₃ system, the value of the ratio $I_{\text{ion}}^{\text{H}_2\text{O}} / I_{\text{ion}}$ shows that, before water admission, the amounts of linear NCO^- present on the surface is five times higher than that of ionic NCO^- . For Pt-Ba/Al₂O₃, small amount of linear NCO^- remains after interaction with 5 mbar of water (Fig. 6A, curve f). So, for Pt-Ba/Al₂O₃ the evaluation of the ratio between the amounts of linear and ionic isocyanates before water admission needs also the estimation of the integrated intensities of the bands related to linear isocyanates before and after H_2O interaction (I_{lin} and $I_{\text{lin}}^{\text{H}_2\text{O}}$, respectively). The ratio $I_{\text{ion}}^{\text{H}_2\text{O}} / I_{\text{ion}}$ is about 1.4, the ratio $I_{\text{lin}} / I_{\text{lin}}^{\text{H}_2\text{O}}$ is about 1.3. These data show that the amounts of linear and ionic NCO^- present on the surface of Pt-Ba/Al₂O₃ catalyst before the water admission are comparable.

The ammonia effect on the NCO^- bands for Pt-Ba/Al₂O₃ (Figure 6B) and Pt-K/Al₂O₃ (not reported) is the same observed for water. As reported for nitrates, the transformation is slower than that observed for water. Indeed, curve "d" in Figure 6B is obtained immediately after the admission of 5 mbar of ammonia, curve "e" after 2h of interaction with 5 mbar of ammonia: the erosion of band at 2230 cm⁻¹ is definitely marked after 2h but not so marked as in the case of water. After 2h of contact the peaks at 3372, 3303 and 3235 cm⁻¹ related to molecular adsorbed ammonia do not change, but the very broad band in the region 3600-2800 cm⁻¹ related to hydroxyl groups formed by dissociative chemisorption of NH₃ markedly increases. As in the case of water, the experiments clearly demonstrate that the dissociative chemisorption of ammonia and not molecularly adsorbed ammonia causes the transformation of the linearly bonded NCO^- into the ionic ones.

Nature and distribution of surface sites and adsorbed species

FT-IR experiments clearly demonstrate that the dissociative chemisorption of water and ammonia causes the transformation of bidentate nitrates and linearly bonded NCO^- into nitrates and isocyanates with a flat geometry on the surface that we call ionic species in order to define species very similar to that found in the corresponding inorganic salts.

The same behavior was observed in literature for ZrO₂ sulfated systems (see ref.³⁹ and references therein): surface hydration of the solid affects the structure and, consequently, the IR spectra of surface sulfates. In fact, on hydrated surface, sulfates have been reported to be mainly in a ionic configuration resembling that of inorganic (bidentate) sulfato-complexes, whereas on dehydrated surfaces the sulfates tends to acquire a configuration that resembles the configuration of the organic sulfonic derivatives.

Both nitrates and isocyanates show high thermal stability. Therefore the effect of water is observable also at higher temperature up to 350 °C on nitrates: the extent of transformation decreases on increasing temperature in relation to the decreased surface hydroxylation. The same was not verified for isocyanates because hydrolysis reactions occur. As for ammonia at high

temperature, it reduces nitrates, so we studied only the effect at RT for all the species considered.

On the basis of the obtained results, it is possible to hypothesize that the dissociative chemisorption of water and ammonia takes place in a competitive way on surface sites on which bidentate nitrates and linearly bonded NCO⁻ are formed. Consequently, these species are dislocated, remaining on surface portions suitable for the formation of species with a flat geometry. In fact, we remember that at the end of the storage, the fraction of K and Ba sites involved in the NO_x storage are close to 40% and 20%, respectively. As a consequence, at the end of the storage, a large part of the K or Ba surface sites are free from nitrates.

The phenomenon described could induce to the erroneous thinking that bidentate nitrates and linear isocyanates are adsorbed on surface sites with dehydrated surrounding, the ionic species on surface sites with hydroxyls in the surrounding. This is not the case, as demonstrated by the surface conditions at the end of NO_x storage and of the reduction with CO: hydroxyl amounts on both the catalysts are really low, in agreement with the previous outgassing at 500 °C. The hydroxyls present are mainly isolated and on the surface both ionic and bidentate/linear species are present.

It is reasonable that the sites on which the competitive chemisorption of water and ammonia occurs are the most reactive ones, thus edge, corner or kink sites. Consequently, it is reasonable that these are the sites on which bidentate nitrates and linear isocyanates are preferentially formed. As a matter of fact, at the end of the storage Pt-Ba/Al₂O₃ catalyst shows mainly ionic nitrates, while Pt-K/Al₂O₃ shows bidentate and ionic nitrates in comparable amounts. Thus, it is possible to conclude that Pt-Ba/Al₂O₃ catalyst shows a lower amount of surface defect sites like edges, corners and kinks with respect to Pt-K/Al₂O₃. In agreement, isocyanate species at the end of storage and reduction with CO are mainly linear, and so formed on defect sites, on Pt-K/Al₂O₃ catalyst, while they are linear and ionic in comparable amounts on Pt-Ba/Al₂O₃ system. Taking into account that for these catalysts bidentate nitrates are chelating and not bridged nitrates, the fact that, before water admission, on Pt-K/Al₂O₃ nitrates are comparable to ionic nitrates, otherwise linear isocyanates are not comparable, but predominant on ionic isocyanates can be related to the higher steric hindrance of bidentate nitrates with respect to that of linear isocyanates. The same argument explains also the distribution of nitrates and isocyanates on Pt-Ba/Al₂O₃ catalyst: the higher steric hindrance of nitrates with respect to isocyanates makes, before water admission, the bidentate nitrates predominant on the ionic ones, but linear NCO⁻ amount equal to that of ionic NCO⁻.

Conclusions

The aim of this work was to investigate the effect of H₂O and NH₃ at room and higher temperature on different surface species formed on Pt-Ba/Al₂O₃ and Pt-K/Al₂O₃ NSR catalysts during storage-reduction cycles. The surface species considered and affected by water and ammonia are nitrates, formed during the NO_x storage step and isocyanates, which are seen to be intermediates in N₂ production during reduction by CO. We found out a common thread that bounds the behavior of these surface species: the dissociative chemisorption of water and

ammonia causes the transformation of bidentate nitrates and of linearly bonded NCO⁻ into nitrates and isocyanates, respectively, with a flat geometry on the surface that we call ionic species. It was possible to hypothesize that the dissociative chemisorption of water and ammonia takes place in a competitive way on surface sites on which bidentate nitrates and linearly bonded NCO⁻ are formed. Consequently, these species are dislocated, remaining on surface portions suitable for the formation of species with a flat geometry.

Notably, the effects of the dissociative chemisorption of water and ammonia allows the identification of surface defect sites like edges, corners and kinks as the defect sites on which bidentate nitrates and linear isocyanates are preferentially formed. On the other hand, it is likely that ionic species are formed on terrace sites. Besides, this study also support the assignment of the two NCO⁻ species observed on Pt-Ba/Al₂O₃ and Pt-K/Al₂O₃ catalysts to the v_{asym}(NCO) modes of two species both adsorbed over different Ba or K sites, in contrast with the assignments found in the literature.

Notes and references

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