

Spectroscopic evidence for the mode of action of alkali promoters in Pt-catalyzed de-NO_x chemistry

S. Koukiou^a, M. Konsolakis^a, R.M. Lambert^b, I.V. Yentekakis^{a,*}

^aLaboratory of Physical Chemistry and Chemical Processes, Department of Sciences, Technical University of Crete, 73100 Chania, Crete, Greece

^bChemistry Department, Cambridge University, Cambridge CB2 1EW, UK

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Abstract

The interaction of NO with sodium-dosed Pt(Na)/ γ -Al₂O₃ catalysts was studied by means of diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). With increasing sodium loading, pronounced and progressive red shifts of the N–O stretching frequency associated with molecular NO adsorbed on the Pt component were observed. This decrease in $\nu(\text{NO})$ correlates with enhancement of NO dissociation at higher temperatures on Na-promoted Pt catalysts under conditions where clean Pt is almost ineffective. These spectroscopic observations provide a clear and consistent explanation for the recently reported very strong promotion by alkalis of the performance of supported Pt catalysts in de-NO_x chemistry [I.V. Yentekakis, M. Konsolakis, R.M. Lambert, N. Macleod, L. Nalbandian, Appl. Catal. B 22 (1999) 123; I.V. Yentekakis, V. Tellou, G. Botzolaki, I.A. Rapakousios, Appl. Catal. B 56 (2005) 229].

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1. Introduction

We recently showed that the de-NO_x catalytic chemistry of Pt-group metals can be very substantially promoted by electropositive promoters (alkalis and alkaline earths) [1–8]. Very large enhancements in the NO reduction rate, by up to two orders of magnitude, accompanied by substantial improvements in N₂ selectivity were achieved with alkali-modified Pt or Pd (0.5 wt% on γ -Al₂O₃) for model TWC reactions such as NO + C₃H₆ [1–4] and NO + CO [5]. Moreover, pronounced beneficial effects on both de-NO_x efficiency and N₂-selectivity were also achieved with Na-promoted Pt/ γ -Al₂O₃ catalysts operated under simulated automotive exhaust conditions [6], and under lean burn conditions [7]. These striking results are of potential practical significance with respect to the development of novel materials formulations for catalytic converters in which only one platinum group metal need be used; such systems offer the additional benefit of easier precious metal recycling, compared to current formulations [8]. Previously, we

proposed that the observed alkali promotion of activity and nitrogen selectivity in de-NO_x catalysis were due to alkali-induced strengthening of the metal-NO bond and the consequent dissociation of NO molecules adsorbed on the platinum metal component of the catalyst. Here, by means of *in situ* DRIFTS, we present evidence that is consistent with this hypothesis.

2. Experimental

2.1. Catalyst preparation

The γ -Al₂O₃ support (Aldrich, BET surface area of 155 m²/g) was impregnated in a solution of Pt(NH₃)₂(NO₂)₂ so as to ultimately yield a 0.5 wt% Pt/ γ -Al₂O₃ catalyst. The resulting material was dried in air (12 h, 120 °C) and divided into three batches, two of which were subsequently impregnated in solutions containing NaNO₃ in order to ultimately yield Pt(Na)/ γ -Al₂O₃ catalysts containing 5.0 and 10.0 wt% Na—hereafter denoted Pt(Na5)/ γ -Al₂O₃ and Pt(Na10)/ γ -Al₂O₃, respectively. These precursors were dried overnight at 120 °C, then calcined in air at 500 °C for 12 h. A reference Na/Al₂O₃ sample (10 wt% Na loading) was also prepared following the same general

* Corresponding author. Tel.: +30 28210 37752; fax: +30 28210 37843.

E-mail address: yentek@science.tuc.gr (I.V. Yentekakis).

procedure. The Na-loadings were chosen by reference to our earlier work on Na promotion of Pt/Al₂O₃ catalysts used for NO reduction by C₃H₆ [1]; it was found that the optimal Na loading was in the range 4–10 wt% Na.

The issues of promoter distribution between support and metal and of actual promoter coverage of the metal component are, of course, common and generally intractable problems in this field. If one assumes that all the promoter is present at the surface and distributed uniformly over the entire available surface area (Pt + γ -Al₂O₃) without any incorporation into the bulk, upper limits for the nominal sodium fractional coverage of 0.25 and 0.5 are calculated for the catalysts with 5 and 10 wt% Na loadings, respectively. This is at least consistent with earlier XPS studies on similar Na-promoted supported catalysts [2], showed a monotonically increasing Na coverage of the catalyst with increasing Na-loading. However, the actual Na coverages on the Pt component were probably substantially less than the above nominal values as much of the promoter phase was likely present as three-dimensional crystallites [9].

2.2. FT-IR studies

Diffuse reflectance IR spectra were collected using an Excalibur spectrometer FTS 3000, equipped with a MCT detector cooled by liquid nitrogen and an environmental cell (Specac) which provided inlet and outlet gas stream lines and sample temperature control up to 600 °C. Infrared spectra were obtained at a resolution of 2 cm⁻¹ by accumulating 64 scans. During IR measurements the external optics were continuously purged by CO₂-free dry air generated in an air purifier system (Claind Italy, CO₂-PUR model). About 80 mg of the powdered catalyst sample was loaded into the IR chamber and its surface carefully flattened in order to optimize the intensity of the reflected IR beam.

He-diluted Air Liquide certified gas mixtures (7.83% NO, 20.7% O₂, 20% H₂) were used and delivered to the DRIFTS cell by mass flow meters (MKS type 247) at 1 bar and a total flow rate of 60 cm³/min. The experimental protocol for acquisition of IR spectra was as follows:

- (i) Sample pre-treatment (to remove pre-adsorbed species):
 - Step i-1: heat to 400 °C (20 °C/min) with 20.7% O₂ (in He) flow. Hold at final temperature for 30 min.
 - Step i-2: purge with He flow at 400 °C for 30 min.
 - Step i-3: reduce with 20% H₂ (in He) flow at 400 °C for 1 h.
 - Step i-4: purge with He at 400 °C for 30 min.
 - Step i-5: return to ambient temperature (27 °C) under He flow.
- (ii) NO adsorption and DRIFT spectra acquisition:
 - Step ii-1: background spectra acquisition at 27 °C under He flow.
 - Step ii-2: adsorption of NO at 27 °C for 1 min under 7.83% NO (in He) flow; spectral acquisition (64 scans; 2 cm⁻¹ resolution).
- (iii) Change sample and repeat above protocol.

In order to investigate possible time dependent effects, the following additional measurements were made. The above protocol was followed, except for step ii-2. Instead, the time of exposure to NO was progressively increased from 1 to 5, 10, 20, 40 and 60 min in order to investigate the effect of prolonged NO adsorption on the resulting NO_x adspecies. In each case, the IR chamber was then purged with He and the temperature was increased in steps of 100 °C to a maximum of 400 °C in order to investigate the thermal stability of these species; spectra being acquired with the “hot” sample in each case.

3. Results and discussion

Fig. 1A–E shows spectra resulting from the interaction of NO with pure γ -Al₂O₃, Na/ γ -Al₂O₃, Pt/ γ -Al₂O₃, Pt(Na5)/ γ -Al₂O₃ and Pt(Na10)/ γ -Al₂O₃ samples, respectively. Bands appearing in the 1650–1200 cm⁻¹ region may be assigned to nitrite/nitrate and nitro species on the support [10–18]. Specifically, the low frequency bands at 1230–1260 and 1330 cm⁻¹ can be attributed to bridging nitrite [10,11,15–18] or chelating nitro species [14,19]; the band at \sim 1260 cm⁻¹, which appeared on Na-promoted samples only, can be assigned to a nitrite ion (NO₂⁻) [10,13]. The remaining bands at 1615, 1580, 1565 and 1500 cm⁻¹ are attributed to various types of nitrates (bridging, bidentate and monodentate) adsorbed on Al₂O₃ carrier [10–18]. These nitrates are also expected to have an additional mode in the

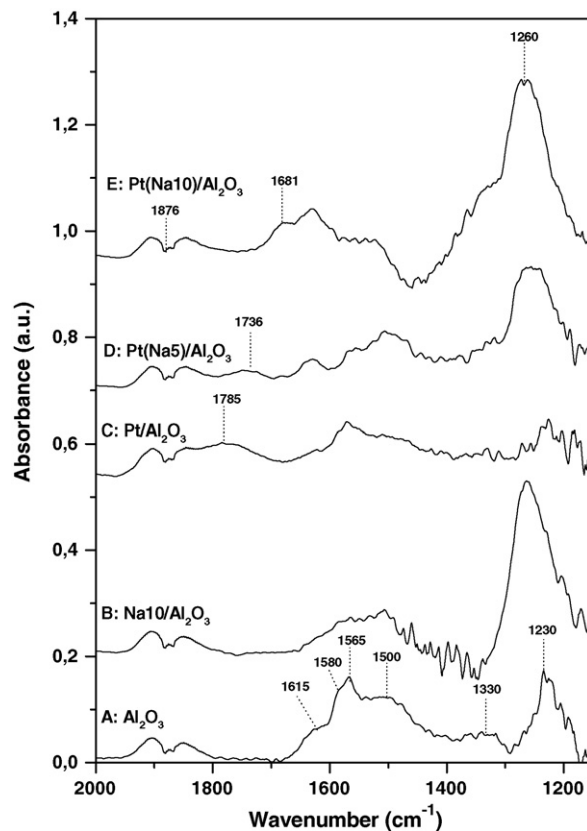


Fig. 1. DRIFT spectra obtained on γ -Al₂O₃ (A), 10 wt%Na/ γ -Al₂O₃ (B), Pt/ γ -Al₂O₃ (C), Pt(Na5)/ γ -Al₂O₃ (D) and Pt(Na10)/ γ -Al₂O₃ (E) samples after NO adsorption for 1 min at 27 °C. Feed: 7.83% NO in He; total flow: 60 cm³/min.

low frequency region (1200–1330 cm^{-1}). Table 1 summarises all the observed bands and the corresponding assignments.

It is apparent from Fig. 1 that for all samples broadly similar features ascribable to support-adsorbed species appear in the region 1650–1200 cm^{-1} . Differences in the populations of these species are not expected to be of primary significance with respect to the SCR properties of supported Pt catalysts under promotion by alkalis for the following reasons. A detailed comparison of the effects of alkali promotion on conventionally supported (Pt/ γ - Al_2O_3) and unsupported (Pt thin film, electrochemically promoted) catalysts has been reported [20]. It was found that the responses to alkali promotion of these two very different systems mirrored each other. In the case of electrochemically promoted thin film catalyst there can be no doubt that the observed promotion was entirely due to alkali on the Pt surface. Therefore, we may reasonably conclude that in the present case promotion is principally due to the effect of Na on the active metal component, rather than on the support. In this connection, it should also be noted that Burch et al. have established that NO reduction by propene takes place exclusively on Pt metal sites [21].

We now consider the surface species present on the Pt component of the various samples which exhibit bands at $>1650 \text{ cm}^{-1}$, whereas no such bands appear for the pure Al_2O_3 and Pt-free $\text{Na}/\text{Al}_2\text{O}_3$ samples, as might have been expected. In contrast, all the Pt-containing samples were characterized by the appearance of weak bands in this spectral region, which may be reasonably attributed to NO_x -derived surface species present on the platinum component. These results are shown with greater clarity in Fig. 2 which depicts background corrected spectra B, C, D and E derived from Fig. 1 by subtraction of spectrum A (pure Al_2O_3). The low intensity of NO bands, compared to CO, obtained from Pt/ SiO_2 has been noted and discussed previously; the reasons for this behaviour

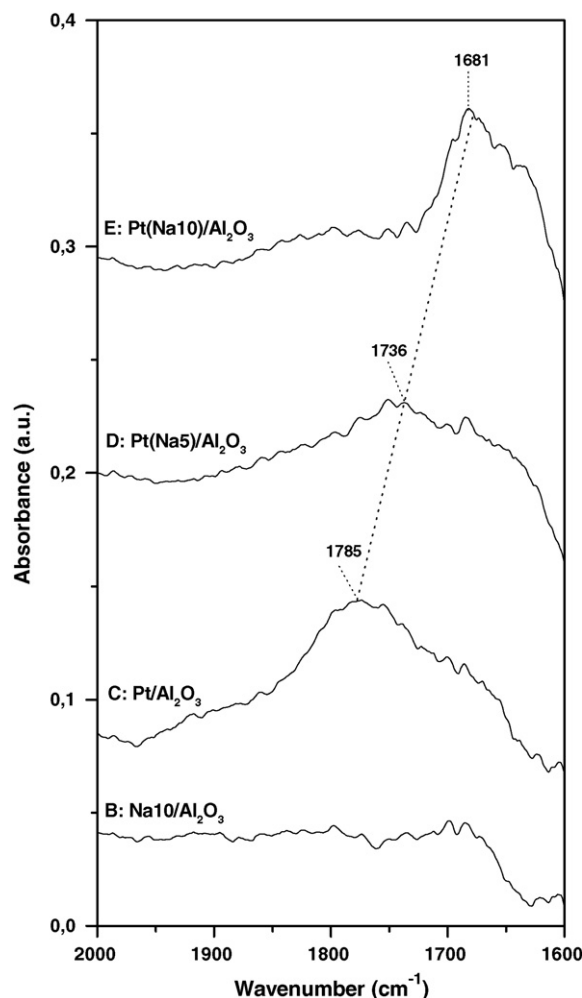


Fig. 2. Expanded scale DRIFT spectra for the region 2000–1600 cm^{-1} obtained with 10 wt% $\text{Na}/\gamma\text{-Al}_2\text{O}_3$ (B), $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ (C), $\text{Pt}(\text{Na}5)/\gamma\text{-Al}_2\text{O}_3$ (D) and $\text{Pt}(\text{Na}10)/\gamma\text{-Al}_2\text{O}_3$ (E) samples after NO adsorption for 1 min at 27 °C. The spectra are derived from the corresponding spectra of Fig. 1 by subtraction of spectrum A (pure Al_2O_3). See text for discussion.

Table 1

Assignments of IR bands for surface species observed on Al_2O_3 , $\text{Pt}/\text{Al}_2\text{O}_3$ and sodium-modified $\text{Pt}(\text{Na})/\text{Al}_2\text{O}_3$ samples during NO adsorption

Surface species	Structure	Peak position (cm^{-1})	Infrared vibration	References
Gas phase NO molecules	N–O	1876	$\nu(\text{N–O})$	[10]
Linear or bent NO on Pt	M–N–O	1680–1780	$\nu(\text{N–O})$	[11,22–25]
Ionic nitrates	NO_3^-	1778	Combination band	[34,35]
Bridging nitrate	$(\text{M–O})_2\text{=NO}$	1615–1620 1200–1300	$\nu(\text{N=O})$ $\nu(\text{NO}_2, \text{as})$	[10–18]
Bidentate nitrate	$\text{M–O}_2\text{NO}$	1555–1585 1200–1300	$\nu(\text{N=O})$ $\nu(\text{NO}_2, \text{as})$	
Monodentate nitrate	M–O–NO_2	1500–1510 1250–1330	$\nu(\text{NO}_2, \text{as})$ $\nu(\text{NO}_2, \text{s})$	
Chelating nitro or bridging nitrite	$(\text{M–O}_2)\text{=N}$ or $(\text{M–O})_2\text{=N}$	1324 1230	$\nu(\text{NO}_2, \text{as})$ $\nu(\text{NO}_2, \text{s})$	[10,11,14–19]
Nitro compounds	M–N–O_2	1415 1315–1350	$\nu(\text{NO}_2, \text{as})$ $\nu(\text{NO}_2, \text{s})$	[10,13,15]
Linear nitrite	M–O–N–O	1436	$\nu(\text{N=O})$	[19]
Nitrite ion (NO_2^-)	NO_2^-	1260	$\nu(\text{NO}_2, \text{as})$	[10,13]
Ionic NO_2 species	M–NO_2^-	~ 1440 1324	$\nu(\text{N=O})$ $\nu(\text{N–O})$	[17,32,33]

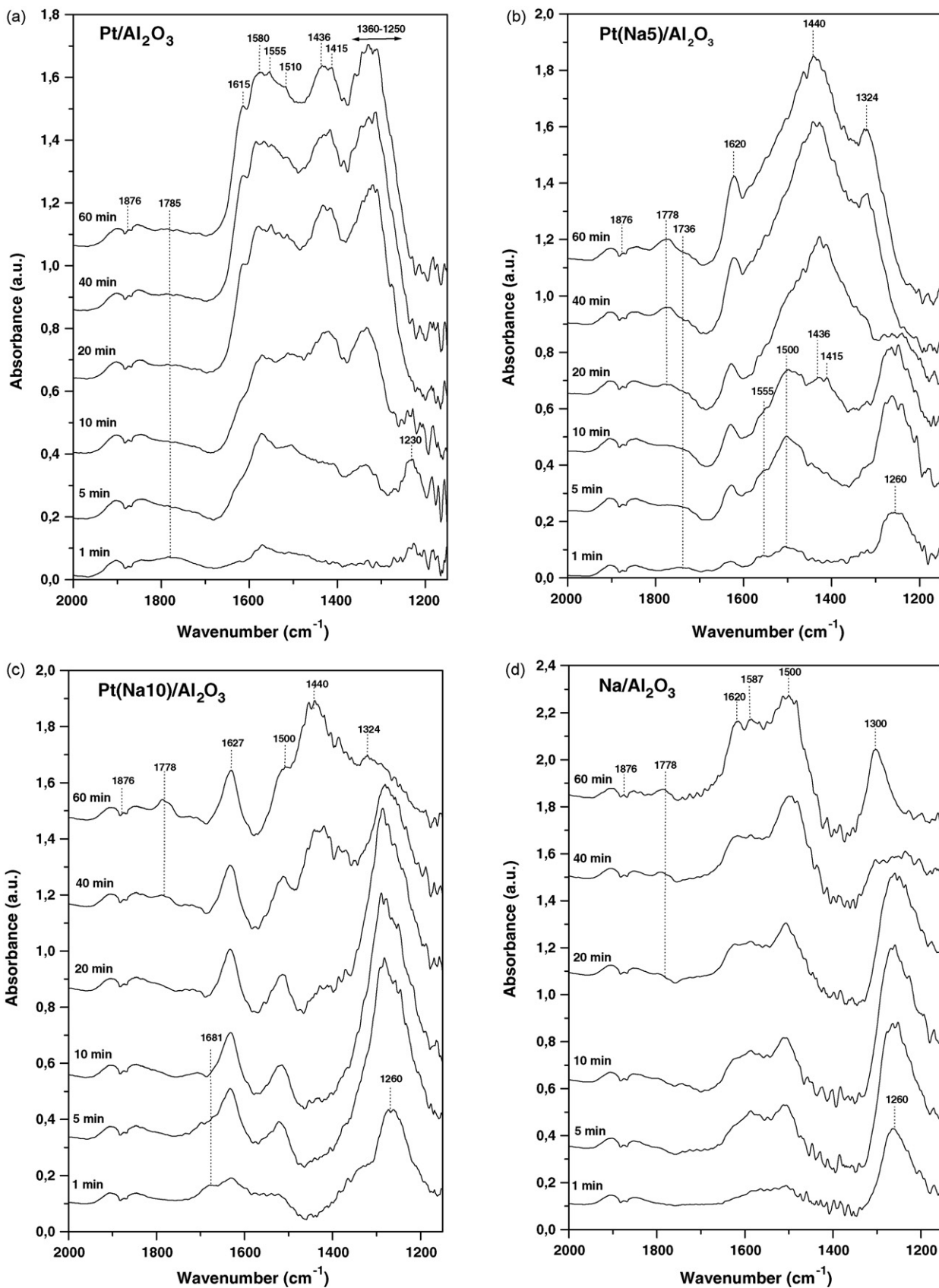


Fig. 3. DRIFT spectra obtained during NO adsorption on (a) Pt/ Al_2O_3 , (b) Pt(Na5)/ Al_2O_3 , (c) Pt(Na10)/ Al_2O_3 and (d) Na/ Al_2O_3 samples at 27 °C, as a function of time of exposure to NO. FT-IR chamber feed: 7.83% NO in He with a total flow of 60 cm^3/min .

are not well understood [22]. The bands observed here correspond to the N–O stretch of linear or bent molecular NO species adsorbed on Pt sites [11,22–25]. The Pt/Al₂O₃ spectra exhibit a very weak band at 1785 cm⁻¹ assigned to linear NO [11,23]. Strikingly, increasing Na promotion (Pt(Na5)/Al₂O₃ and Pt(Na10)/Al₂O₃, spectra D and E in Fig. 2) causes the development of bands at progressively lower wave numbers: the pronounced 1681 cm⁻¹ band observed at the highest Na loading is of particular interest. As pointed out long ago by Gardner et al. [25] who carried out detailed single crystal studies on the Pt–NO system, the assignment of adsorption sites and bond orders is not straightforward. More recent DFT calculations on Pt{100}–NO associate bands at 1595–1640 with a species having an N–O bond length of 121 pm [26]. This corresponds to an N–O bond order of 2, i.e. a negatively charged adsorbate (NO^{δ-}) with increased electron density in the π* antibonding orbital. We shall argue below that this electronic effect is the direct consequence of alkali promotion which activates the N–O bond towards dissociation, thus triggering subsequent catalytic chemistry.

The effect of co-adsorbed sodium on the bonding of chemisorbed NO may be discussed in terms of the model proposed by Blyholder many years ago [27]. According to this view, substrate-mediated electron transfer can be thought of as taking place between an electropositive adsorbate (such as an alkali atom) and the NO antibonding π* orbital as a result of alkali-enhanced d–π electron back donation. Though of some use in qualitative discussions of (say) NO + Na co-adsorption on Pt under vacuum conditions, this view is not really appropriate to an understanding of what occurs at the surface of a practical catalyst operating at elevated pressure and temperature. In practical systems, there can be no doubt that the alkali promoter is present in an ionic state so it is appropriate to use the rigorous model developed by Lang et al. [28] who showed that the inhomogeneous electric field associated with adsorbed alkali ions acts to depress the energy of the antibonding π* orbital of electron-accepting co-adsorbates (CO, NO) below the metal Fermi level. In the present case, the resulting metal → adsorbate charge transfer acts to weaken the N–O bond, red-shifting its vibration frequency and promoting its dissociation, in very good accord with present observations. It could be argued that the red shifts we observe are due to alkali-induced changes in the relative populations of various forms of adsorbed NO rather than weakening of the N–O bond in a single type of adsorbed NO. However, both experimental and theoretical studies carried out on a variety of well defined metal surfaces (Co, Pt, Pd, Rh, etc.) unequivocally demonstrate that co-adsorbed alkalis act electronically to weaken the N–O bond and red shift ν(NO); see for example [29–31]. Accordingly, our proposed explanation is not merely plausible but very well founded.

Fig. 3 shows the effect of prolonged NO adsorption on the formation of NO_x adspecies for Pt/Al₂O₃ (Fig. 3a), Pt(Na5)/Al₂O₃ (Fig. 3b), Pt(Na10)/Al₂O₃ (Fig. 3c) and Na/Al₂O₃ (Fig. 3d). Interestingly, the time dependence of the bands at 1785, 1736 and 1681 cm⁻¹ for the Pt/Al₂O₃, Pt(Na5)/Al₂O₃ and Pt(Na10)/Al₂O₃ samples, respectively, assigned to the N–O

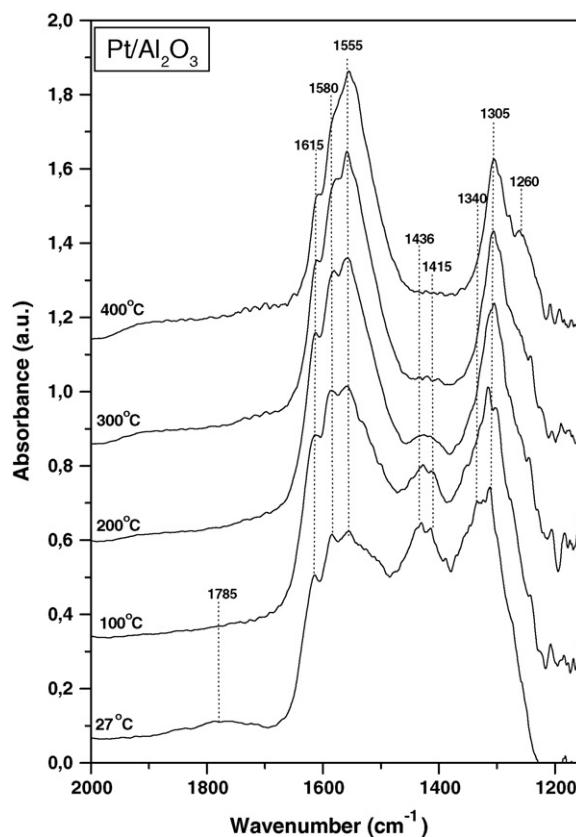


Fig. 4. DRIFT spectra of Pt/Al₂O₃ sample after interaction with NO for 60 min at 27 °C and subsequent stepwise increase of temperature in He flow of 60 cm³/min.

stretch of linear or bent molecular NO species adsorbed on Pt sites (Table 1) is noticeably different in each case. Thus, for Pt/Al₂O₃ the intensity of the N–O stretch (1785 cm⁻¹, Fig. 3a) remains almost constant up to 60 min of NO exposure, that of the bands at 1736 and 1681 cm⁻¹ over the Na-modified samples, Pt(Na5)/Al₂O₃ and Pt(Na10)/Al₂O₃, respectively, progressively diminished with increasing exposure time, eventually disappearing at ~20 and 10 min, respectively. That is, the higher Na loading the more rapidly the band corresponding to the N–O stretch of molecular NO adsorbed on Pt sites was attenuated. This is consistent with progressive population of the Pt surface with atomic oxygen resulting from Na-induced NO dissociation, eventually poisoning adsorption of molecular NO. Finally, Fig. 4 shows that for Pt/Al₂O₃ the intensity of the 1785 cm⁻¹ band was not affected by purging with He at 27 °C. This feature, however, did disappear upon increasing temperature above 100 °C. These observations further support the proposed assignment of these bands and provide further evidence for the proposed mode of action of Na promoter on the surface chemistry of Pt/NO. (An account of the behaviour of other bands that are peripheral to the principal message of this paper is given in the Appendix A.)

4. Conclusions

- (1) The N–O stretching frequency for chemisorbed NO on Na-modified Pt sites, shifts to progressively lower frequency

with increasing Na loading. At the highest loading a 1680 cm^{-1} species is observed corresponding to an activated $\text{NO}^{\delta-}$ species with bond order 2. This provides the first direct spectroscopic evidence for weakening of the N–O bond induced by alkali promotion of a practical dispersed platinum metal catalyst.

- (2) This activation of the N–O bond towards dissociation provides a basis for understanding the recently reported strong promotional effect of alkalis in de-NO_x catalytic chemistry of platinum group metals.

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Appendix A

Inspection of the spectra in Fig. 3 indicates that significant differences also exist in the $1650\text{--}1200\text{ cm}^{-1}$ region between the Na-free (Fig. 3a) and Na-dosed samples (Fig. 3b–d). Specifically, the population of nitro/nitrite species (band at 1260 cm^{-1}) is significantly higher on Na-dosed samples. The intensity of this band initially increased with NO exposure time, passed through a maximum and eventually decreased at longer times (typically $t > \sim 10\text{ min}$). At this stage, new bands appeared at ~ 1440 and 1778 cm^{-1} their intensity increasing with time; the broad feature at $\sim 1440\text{ cm}^{-1}$ may be assigned to a dispersed sodium nitrite phase. Similar bands have been observed during NO or NO₂ adsorption on Ba containing samples [17,32,33]. The band at 1778 cm^{-1} can be assigned to nitrate ions associated with sodium: the absence of this band in the spectra of Na-free sample (Fig. 3a) and its appearance in those of all the Na-containing samples (Fig. 3b–d) support this view. Inspection of the spectra shown in Fig. 4, where the temperature of the Pt/Al₂O₃ sample was increased up to $400\text{ }^{\circ}\text{C}$ after NO adsorption for 60 min at $27\text{ }^{\circ}\text{C}$, shows that bands at 1415 cm^{-1} (nitro compounds associated with Al sites; Table 1) and 1436 cm^{-1} (linear nitrites on Al₂O₃; Table 1) are eliminated at $\sim 300\text{ }^{\circ}\text{C}$. In contrast, the bands at 1778 and $\sim 1440\text{ cm}^{-1}$ observed during similar experiments with Na-containing samples (data not shown here) persisted even at

$400\text{ }^{\circ}\text{C}$, consistent with their assignment to stable ionic compounds of sodium.

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