Catalysis Today 155 (2010) 172–176

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

# *In situ* PM-IRRAS study of powder catalyst: Dynamic evolutions of species on catalyst and in gas phase during $NO_x$ storage-reduction

Eva Roedel, Atsushi Urakawa *, Alfons Baiker *

*Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Hönggerberg, HCI, CH-8093 Zurich, Switzerland*

ARTICLE INFO

*Article history:*
Available online 29 December 2009

*Keywords:*
PM-IRRAS
Powder catalyst
*In situ* spectroscopy
Time-resolution
$NO_x$ storage-reduction

ABSTRACT

The potential of polarization-modulation infrared reflection-absorption spectroscopy (PM-IRRAS) for *in situ* and time-resolved studies using powder samples is demonstrated using as an example the $NO_x$ storage-reduction behaviour of a Pt-Ba/$Al_2O_3$ powder catalyst. The unique feature of PM-IRRAS, the simultaneous but separate detection of gas phase species and species on the catalyst surface, is illustrated. Bands due to the powder prominently appeared in the gas phase spectra due to transmittance and absorption of IR-light by the solid. The difference in the appearance of powder bands in the gas phase and surface spectra was explained by the distinct local sensitivity in the gas phase and surface spectra for powder samples and also by optoelectronic effects caused by the photoelastic modulator. The study shows that PM-IRRAS is not only suitable for *in situ* mechanistic studies on idealized model film catalysts, but also for the investigation of technically more relevant powder catalysts.

## 1. Introduction

Polarization-modulation infrared reflection-absorption spectroscopy (PM-IRRAS), based on external reflection of polarized infrared light, is a powerful vibrational spectroscopic method which allows very sensitive detection of species residing at gas–solid [1–3], solid–liquid [4–9], and gas–liquid [10,11] interfaces. The main advantages of the technique are the high sensitivity, which is important for time-resolved studies, and the possibility of *in situ* studies under technically relevant conditions, i.e. under pressure (even liquid) at high temperature (measurements up to 600 K have been reported). Recently, the potential of PM-IRRAS has been extended by monitoring not only surface species but also gas- and liquid-phase species with a good time-resolution (ca. 1 s) [12]. Although the technique can be applied for studying various surface processes, the flatness of samples is a prerequisite to achieve high detection sensitivity towards surface species, which sometimes precludes its use for investigating more realistic samples with rough surfaces. In this study, we present the first time-resolved *in situ* PM-IRRAS study of a powder sample with simultaneous detection of species in gas phase and on the powder surface. Our main aim is to examine the suitability and spectral features of PM-IRRAS when applied to powder samples. As a test system we chose the $NO_x$ storage-reduction (NSR) behaviour of a Pt-Ba/$Al_2O_3$ powder catalyst.

NSR has gained considerable attention because it is one of the most promising methods for $NO_x$ removal from lean engine exhausts [13–15]. NSR utilizes periodic switching between fuel-lean (oxidative atmosphere) and fuel-rich (reductive atmosphere) conditions. During fuel-lean periods, NO is oxidized to $NO_2$ over a noble metal component, such as Pt, and stored on an alkali or alkaline-earth metal component of the catalysts, such as Ba, in the form of nitrates. During short fuel-rich periods, the stored $NO_x$ is released and reduced to $N_2$ over the noble metal. The Ba component is regenerated for $NO_x$ storage during rich periods. A variety of Ba species (e.g. nitrite, nitrate, carbonate, oxide, peroxide, and hydroxide), gas phase species (e.g. NO, $NO_2$, $N_2O$, $NH_3$, $H_2O$, CO, and $CO_2$), and even support materials (e.g. $Al_2O_3$ and $CeO_2$), particularly their surfaces, are involved in the chemical transformations. The detection and identification of involved chemical processes occurring on the catalyst and also in the gas phase are crucial to understand the reaction mechanism. Here, we studied NSR using a Pt-Ba/$Al_2O_3$ powder sample deposited on an Al wafer in the flow-through PM-IRRAS cell [12]. $H_2$ was used as a model reductant. We demonstrate that PM-IRRAS can be utilized to study dynamic evolutions of species on powder catalysts and in gas phase simultaneously. The unique spectral features and potential problems encountered in data analysis due the use of powder samples are discussed.

---

* Corresponding authors.
*E-mail addresses:* urakawa@chem.ethz.ch (A. Urakawa), baiker@chem.ethz.ch (A. Baiker).

0920-5861/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2009.11.013

## 2. Experimental

### 2.1. Catalyst

The Pt-Ba/$Al_2O_3$ catalyst (weight ratio: Pt:Ba:$Al_2O_3$ = 1:20:100) was prepared by two-nozzle flame spray pyrolysis [16] to control the proximity of the Pt and Ba component, which is critical for good NSR performance particularly for regeneration of the Ba component for $NO_x$ storage. In one flame $Al_2O_3$ particles and in the other flame $BaCO_3$ and Pt particles were formed and mixed at a certain distance. The apparatus and experimental procedure used as well as the catalyst properties are described elsewhere [17].

In order to enhance the adhesion of the catalyst powder on the aluminum wafer which acts as the reflective substrate for PM-IRRAS, a small amount of the catalyst powder (<1 mg) was deposited in small channels (ca. 0.2–0.5 mm width and depth) formed on the aluminum wafer (Fig. 1) to enhance the adhesion and fixation of the catalyst on the wafer under flow conditions.

### 2.2. PM-IRRAS

In brief, PM-IRRAS utilizes light whose polarization is modulated, i.e. repeatedly alternated in time between its *p*- and *s*-polarizations, by means of a photoelastic modulator (PEM). The *p* (parallel) and *s* (perpendicular) directions are defined by their orientation with respect to the plane spanned by the incident and reflected light. Hence with the condition of near-specular reflection, the *s*- and the major component of the *p*-polarizations are parallel and perpendicular to the sample surface, respectively [18]. Upon reflection of infrared light at the surface, ca. 180° phase shift for the *s*-polarization electric field occurs while the phase of the *p*-polarization is only weakly affected by the reflection (when the angle of incidence is 0–80°). Consequently, destructive and constructive interferences of the electric field occur between the incident and reflected *s*- and *p*-polarizations, respectively [18]. Hence, the *p*-polarization contains information about the species on the surface and in the gas phase, whereas the *s*-polarization contains information about only the gas phase species due to destructive interference, i.e. no net electric field at the surface [12]. Division of the measured difference reflectivity ($p - s$) by the sum reflectivity ($p + s$) yields the PM-IRRA surface spectrum, while the sum reflectivity is used to calculate the PM-IRRA gas phase spectrum. Note that the latter is justified due to the much higher concentration of gas phase species compared to surface species. The details of the technique and of the simultaneous detection of surface and gas phase species can be found elsewhere [12,19].

The catalyst powder deposited on the aluminum wafer was placed in the sample holder of the flow-through PM-IRRAS cell with a small volume (ca. 7 ml) and short light path length (25.9 mm) [12]. The cell was located in a Bruker PMA 37 compartment connected to an external beam port of a Bruker Vector 33 Fourier transform infrared spectrometer. The angle of incidence was 80° and the light was focused on a liquid nitrogen-cooled MCT detector. Spectra were recorded at 4 $cm^{-1}$ resolution. The polarization was modulated using PEM at a frequency of 100 kHz with a photoelastic modulator set for half-wave retardation at 1800 $cm^{-1}$.

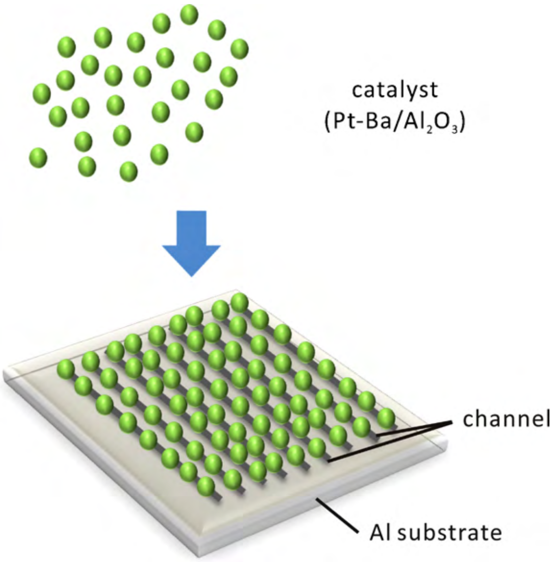

**Fig. 1.** Schematic drawing of the PM-IRRAS sample prepared by the deposition of catalyst powders into the channels on the aluminum substrate.

### 2.3. NSR

Two types of NSR experiments were carried out: (1) NO + $O_2$ (lean) vs. $H_2$ (rich), and (2) $NO_2$ + $O_2$ (lean) vs. $H_2$ (rich). In more detail, the lean atmosphere contained 4700 ppm NO (>99.9 vol.%, PanGas) or 4300 ppm $NO_2$ (>99.9 vol.%, PanGas) and 3.3% $O_2$ (>99.999 vol.%, PanGas) with balance He (>99.999 vol.%, PanGas) and the rich atmosphere contained 3.3% $H_2$ (>99.999 vol.%, PanGas) with balance He (>99.999 vol.%, PanGas). The period lengths were 188 s for lean periods and 62 s for rich periods (total 250 s). All experiments were performed isothermally at 573 K at a total gas flow of 60 ml/min. Prior to spectra recording, the fresh catalyst was exposed to a number of the lean-rich cycles at 573 K until a reproducible concentration response of effluent gas components was attained. 60 spectra were recorded per NSR cycle (15 and 45 spectra for rich and lean, respectively, 250 s per cycle). Finally 60 PM-IRRA spectra of one NSR cycle for surface (catalyst) and gas phase were obtained by averaging 10 NSR cycles to enhance the signal-to-noise ratio. The last spectrum measured during the rich period was taken as internal reference for normalization of surface spectra and absorbance calculation of gas phase spectra. The PM-IRRA surface spectra are presented as normalized PM-IRRA units (obtained by division of the internal reference spectrum) and the gas phase PM-IRRA spectra are presented in absorbance units. Furthermore, the gas phase composition at the cell outlet was analyzed using mass spectrometry (Omnistar, Pfeiffer Vacuum) as well as a chemiluminescence detector (CLD 822 S, Eco Physics).

## 3. Results and discussion

### 3.1. NSR: NO + $O_2$ vs. $H_2$

The PM-IRRA surface (i.e. powder) and gas phase spectra during NSR (NO + $O_2$ vs. $H_2$) are shown in Fig. 2. Clearly, the PM-IRRA surface spectra (Fig. 2a) do not show the gas phase species; the excellent compensation of signals due to gas phase species was confirmed using a powder sample deposited not only on a flat metallic surface but also on a rough surface, i.e. on the channels of the metallic substrate. On the other hand, the PM-IRRA gas phase spectra (Fig. 2b) show all IR-active gas phase species relevant in NSR (NO, $NO_2$, $N_2O$, and $H_2O$) and their evolutions during NSR. However, prominent bands were observed in the region where the bands were present in the surface spectra (Fig. 2a). Interestingly, the bands were slightly red-shifted in the gas phase spectra compared to those in the surface spectra. The appearance of those bands in the gas phase spectra is discussed later in more detail.

Three bands were observed in the PM-IRRA surface spectra (Fig. 2a). The band at ca. 1170 $cm^{-1}$ appeared immediately after switching to the lean (NO + $O_2$) atmosphere, while the emerging of

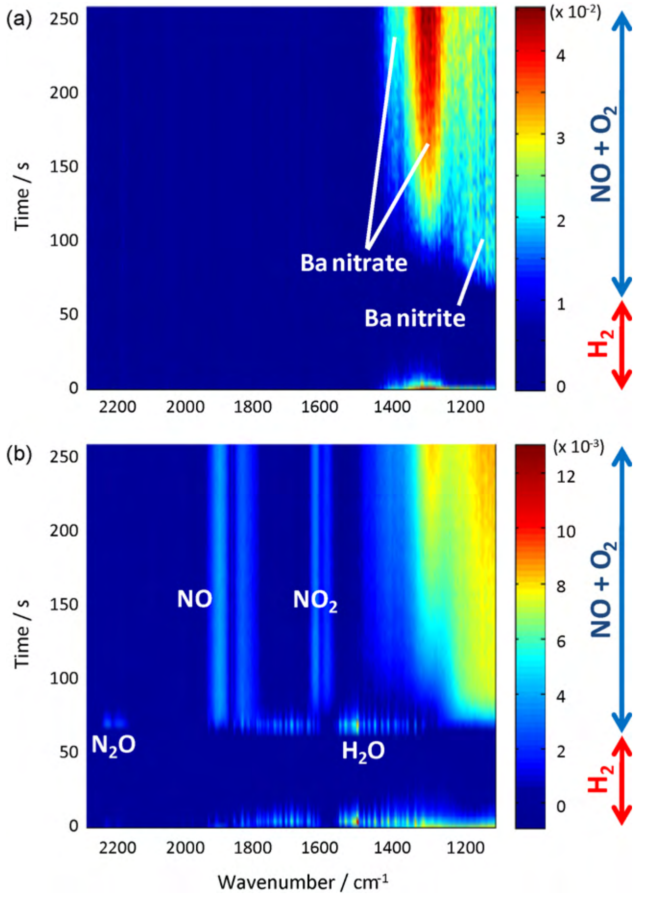

**Fig. 2.** PM-IRRA surface (a) and gas phase (b) spectra during NSR using NO-based lean periods. The units are in the normalized PM-IRRA unit for (a) and absorbance for (b).

the two bands at ca. 1300 and 1420 $cm^{-1}$ was significantly delayed. Apparently, the formation of the band at 1420 $cm^{-1}$ was more delayed, but this is due to the color scale of the figure and the temporal profiles of the two bands were identical when their intensities were normalized. The band at 1170 $cm^{-1}$ is assigned to Ba nitrite and the other two bands at 1300 and 1420 $cm^{-1}$ are assigned to Ba nitrate ($\nu_3$), although the frequencies of 1170 and 1300 $cm^{-1}$ are considerably lower than commonly reported for Ba nitrite and nitrate, respectively [20,21]. The surface Ba nitrate bands, typically observed at ca. 1500 $cm^{-1}$, were not observed. Also no nitrate species adsorbed on the $Al_2O_3$ support was observed, whose band appears typically at ca. 1600 $cm^{-1}$. The absence of bands due to surface adsorbed species indicates that the surface sensitivity is considerably deteriorated by the powder form of the sample, although PM-IRRAS is generally considered as surface sensitive technique.

One of the most promising features of PM-IRRAS on powder samples is the time-resolved monitoring of gas phase and surface (powder) species. Fig. 3 shows the evolutions of selected species in the gas phase and on the surface during NSR. It should be emphasized that the information was obtained separately but simultaneously. Upon switching to lean ($NO + O_2$) atmosphere, $H_2O$ was immediately formed, followed by the formation of $N_2O$ and gradual increase of $NO_2$. On the catalyst, Ba nitrite was formed rapidly during the initial phase of lean periods but then leveled off. On the other hand, the Ba nitrate signal increased gradually and continuously during lean periods. The oxidation of Ba nitrites to Ba nitrates is often reported, and the profiles of Ba nitrite and nitrates indicate the occurrence of such an oxidation process [22,23]. The $H_2O$ formation was largely due to the gas mixing in the PM-IRRAS cell, i.e. coexistence of $O_2$ and $H_2$, and their reaction catalyzed by Pt. Furthermore, the formation of $N_2O$ was also catalyzed by Pt in the reductive atmosphere caused by the coexistence of $O_2$ and $H_2$ as confirmed by employing a Pt film instead of the powder deposited on the substrate under the same NSR conditions (not shown). Moreover, $NH_3$ was not observed in this study (confirmed by IR and MS).

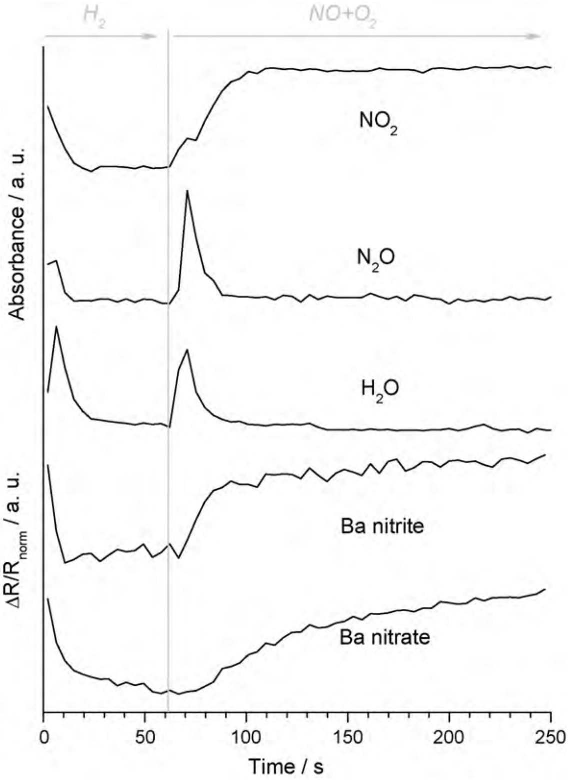

**Fig. 3.** Evolutions of selected species in the gas phase and on the catalyst during NSR using NO-based lean periods. For $NO_2$, $N_2O$, $H_2O$, the evolutions in the gas phase are shown by the absorbance (a.u.) at 1630, 2240, and 1716 $cm^{-1}$, respectively. For Ba nitrite and Ba nitrate, the evolutions on the catalyst are shown in the normalized PM-IRRA unit at 1170 and 1300 $cm^{-1}$, respectively.

The evolutions of the nitrite and nitrate species can be explained by the $NO_x$ species available in the gas phase. At the initial phase of lean periods, the atmosphere is still reductive, as seen by the formation of $H_2O$ and $N_2O$, and NO is not oxidized to $NO_2$. During this phase, largely NO is available and direct storage of NO seems dominating, resulting in the formation of Ba nitrite. When the atmosphere becomes more oxidative, $NO_2$ is stored as Ba nitrate since a sufficient amount of $NO_2$ is available to store it via the common 'nitrate' route [22,24].

During rich periods, Ba nitrite decreased abruptly, while Ba nitrate initially decreased rapidly as the nitrite but then gradually decreased. The fast decomposition of Ba nitrite is in accordance with our previous study showing that the nitrite is merely a surface species and consequently the reduction is fast [25]. The two-step reduction of Ba nitrate may arise from similar origin, e.g. at first reduction of surface Ba nitrate occurs followed by the gradual reduction of bulk Ba nitrate.

The $NO_x$ concentration profiles obtained by PM-IRRAS were identical to those measured using CLD (Fig. 6), although a certain delay of the $NO_x$ concentration response was observed for CLD compared to PM-IRRAS. The advantage of PM-IRRAS for the detection of gas phase species is that they are measured right above the surface and hence the technique is very sensitive and responds spontaneously to the evolved gas phase species, rendering it well-suited for studying the correlation between the evolved surface and gas phase species [12].

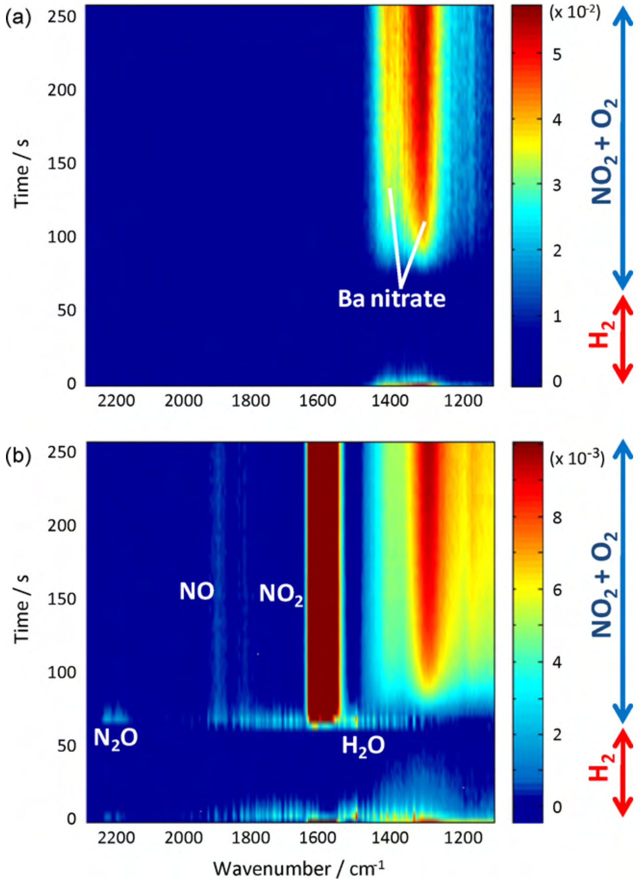

**Fig. 4.** PM-IRRA surface (a) and gas phase (b) spectra during NSR using $NO_2$-based lean periods. The units are in the normalized PM-IRRA unit for (a) and absorbance for (b).

### 3.2. NSR: $NO_2 + O_2$ vs. $H_2$

Fig. 4 shows the PM-IRRA surface and gas phase spectra measured under identical conditions as in Fig. 2 except that NO was replaced by $NO_2$. Clearly, all the relevant gas phase and surface (powder) species could be monitored, their evolutions are shown in Fig. 5. Very similar $H_2O$ and $N_2O$ formation profiles as those in the NO-based lean experiment were observed in the gas phase. Expectedly, Ba nitrate was formed much faster than under the NO-based lean conditions and even faster than nitrite formation. The Ba nitrite profile was somewhat correlated to the concentration of NO in the gas phase and the formation started when sufficient amount of NO was formed in the gas phase. The amount of Ba nitrite (Fig. 4a) was also significantly less, which supports the nitrite formation via the 'NO' route. During rich periods, the two-step reduction, similar to the NO-based NSR, was observed. The accuracy of NO and $NO_2$ evolutions was verified by CLD (Fig. 6).

Similarly to Fig. 2, the gas phase compensation in the PM-IRRA surface spectra was excellent (Fig. 4a) and the PM-IRRA gas phase spectra (Fig. 4b) show remarkable contribution of bands of the surface spectra with slight red-shifts and increase in the absorbance at lower frequency. Possible origins of these observations are discussed in the next section.

### 3.3. General remarks on PM-IRRAS of powder samples

In the present study, a powder sample supported on the channels of the aluminum substrate was investigated by *in situ* time-resolved PM-IRRAS. The PM-IRRA surface spectra showed excellent compensation of gas phase components. The PM-IRRA gas phase spectra showed the evolutions of gas phase components; however they also contained the contributions due to the surface (powder) species with slightly different spectral features (band position and intensity).

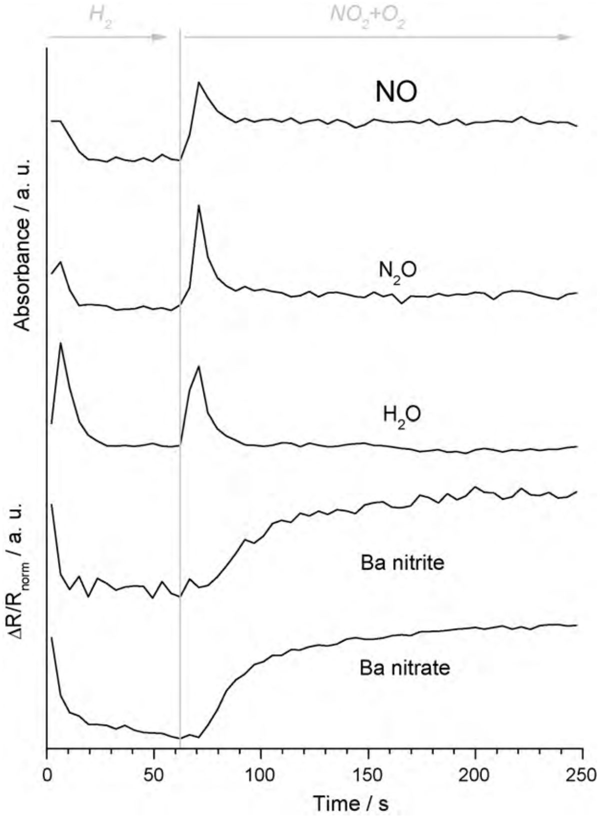

**Fig. 5.** Evolutions of selected species in the gas phase and on the catalyst during NSR using $NO_2$-based lean periods. For NO, $N_2O$, $H_2O$, the evolutions in the gas phase are shown by the absorbance (a.u.) at 1910, 2240, and 1716 $cm^{-1}$, respectively. For Ba nitrite and Ba nitrate, the evolutions on the catalyst are shown in the normalized PM-IRRA unit at 1170 and 1300 $cm^{-1}$, respectively.

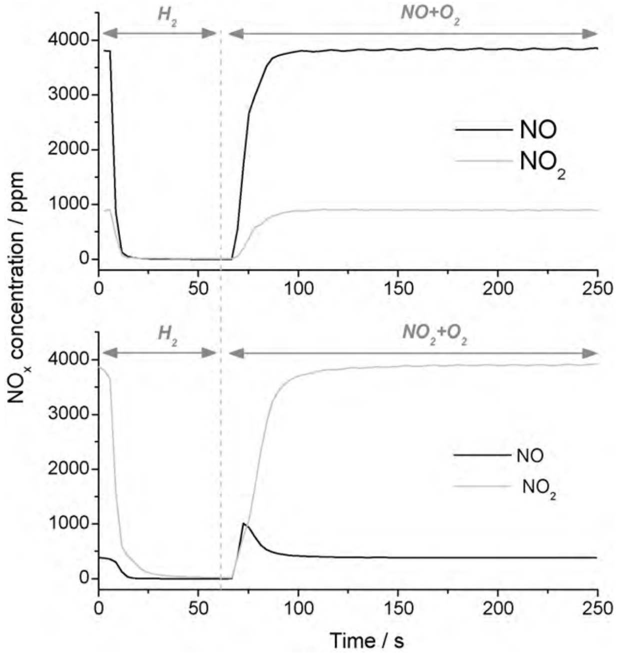

**Fig. 6.** $NO_x$ concentration profiles measured by CLD during NSR using NO-based (upper panel) and $NO_2$-based (lower panel) lean periods.

The excellent compensation of gas phase components while observing a good surface spectrum shows that the chemical information of a powder can be probed by the reflectivity difference ($p - s$ polarization). Most likely, the surface spectrum originates from the region which is in proximity to the surface of the metallic substrate where the PM-IRRAS selection rule is valid.

On the other hand, IR-light transmittance through the sample is possible when powder samples are investigated by PM-IRRAS, which could be evidently recognized by the surface (powder) band components in the gas phase spectra (Figs. 2b and 4b). This effect is important to realize; however it does not disturb the simultaneous monitoring of gas phase and surface species as long as the surface (powder) and gas phase bands do not overlap completely as in this study.

This also implies that the appearance of powder bands may show up differently in the gas phase and surface spectra due to the difference in the probing locations of the two spectra. In the surface spectrum, the region touching or in proximity to the surface in the order of several tenths of nanometers is probed while more bulk components are probed in the gas phase spectrum due to the IR-transmission through the powder. This is especially true when a powder absorbs IR-light weakly and is highly transparent in IR. This could be a reason for the observed red-shifts and also intensity differences.

Another possible cause of these effects is the difference ($p - s$ polarization) reflectivity component present in the gas phase spectrum (generally the sum reflectivity, $p + s$ polarization, is taken) [19]. It is typically negligible but the contribution may no longer be negligible when highly IR-absorbing powder samples are probed. Particularly, the multiplication of the difference reflectivity with the frequency-dependent zeroth order Bessel function, which appears due to the use of PEM, may cause different band appearance in the surface and gas phase spectra. This well explains the consistent red-shift and higher band intensity at lower frequencies when a spectrum is multiplied by a function which is linearly increasing towards lower frequency.

One important aspect in practice is the local sensitivity of the method for powder samples. As we have shown previously by comparing the *ex situ* spectra of powders measured by four different IR techniques (transmission, attenuated total reflection (ATR), diffuse reflectance, and PM-IRRAS), PM-IRRAS is not a surface sensitive technique on an atomic scale in comparison to scattering-based diffuse reflectance configuration [20]. The above-described several tenths of nanometers probing depth for powder samples can show the bulk component of powders more prominently than its outer surface component. This bulk sensitivity of PM-IRRAS for powder samples was also evidenced in this study, i.e. the absence of surface Ba nitrates and also surface nitrates adsorbed on $Al_2O_3$, which are commonly observed in a diffuse reflectance configuration.

## 4. Conclusions

The potential of *in situ* time-resolved PM-IRRAS for the elucidation of the changes occurring in the gas phase and on a powder NSR catalyst (Pt-Ba/$Al_2O_3$) during cycling between lean and rich periods has been investigated. Gas phase species and species on the catalyst could be monitored simultaneously. Excellent compensation of gas phase components was achieved despite the imperfect flatness of the sample. Due to the strong IR-absorption by the powder, the bands due to the powder appeared in the gas phase spectra, whose appearance was somewhat different from the corresponding bands observed in the surface spectra. The difference can be explained by the local sensitivity for powder samples in the gas phase and surface spectra and also by optoelectronic effects caused by the photoelastic modulator. This study may widen the range of PM-IRRAS applicability from an idealized model film catalyst to practically relevant powder catalysts for *in situ* mechanistic studies. Moreover, it can serve as a reference for comparing PM-IRRAS studies on model films with studies on powder catalysts which are more suitable for the investigation of the catalytic behaviour, but are less well defined.

## Acknowledgements

The authors thank Robert Büchel and Prof. Sotiris E. Pratsinis for providing the powder catalyst used for this study. Financial support of this work by ETH Zurich (TH-0906-2) is kindly acknowledged.

## References

[1] A. Hatta, H. Matsumoto, W. Suetaka, Chem. Lett. (1983) 1077.
[2] M.J. Green, B.J. Barner, R.M. Corn, Rev. Sci. Instrum. 62 (1991) 1426.
[3] G. Rupprechter, C. Weilach, J. Phys. Condens. Mater. 20 (2008) 184019.
[4] H. Seki, K. Kunimatsu, W.G. Golden, Appl. Spectrosc. 39 (1985) 437.
[5] K. Ashley, S. Pons, Chem. Rev. 88 (1988) 673.
[6] T. Iwasita, F.C. Nart, Prog. Surf. Sci. 55 (1997) 271.
[7] D.M. Meier, A. Urakawa, A. Baiker, Analyst 134 (2009) 1779.
[8] D.M. Meier, A. Urakawa, A. Baiker, Phys. Chem. Chem. Phys. 11 (2009) 10132.
[9] D.M. Meier, A. Urakawa, R. Mader, A. Baiker, Rev. Sci. Instrum. (2009) 094101.
[10] D. Blaudez, T. Buffeteau, J.C. Cornut, B. Desbat, N. Escafre, M. Pezolet, J.M. Turlet, Appl. Spectrosc. 47 (1993) 869.
[11] S.M. McClure, D.W. Goodman, Chem. Phys. Lett. 469 (2009) 1.
[12] A. Urakawa, T. Bürgi, H.-P. Schläpfer, A. Baiker, J. Chem. Phys. 124 (2006) 054717.
[13] S. Matsumoto, Catal. Today 29 (1996) 43.
[14] W.S. Epling, L.E. Campbell, A. Yezerets, N.W. Currier, J.E. Parks, Catal. Rev. Sci. Eng. 46 (2004) 163.
[15] S. Roy, A. Baiker, Chem. Rev. 109 (2009) 4054.
[16] R. Strobel, L. Mädler, M. Piacentini, M. Maciejewski, A. Baiker, S.E. Pratsinis, Chem. Mater. 18 (2006) 2532.
[17] R. Büchel, R. Strobel, F. Krumeich, A. Baiker, S.E. Pratsinis, J. Catal. 261 (2009) 201.
[18] B.E. Hayden, in: J.T. Yates, Jr., T.E. Madey (Eds.), Vibrational Spectroscopy of Molecules on Surfaces, Plenum Press, New York, 1987.
[19] T. Buffeteau, B. Desbat, J.M. Turlet, Appl. Spectrosc. 45 (1991) 380.
[20] E. Roedel, A. Urakawa, S. Kureti, A. Baiker, Phys. Chem. Chem. Phys. 10 (2008) 6190.
[21] H. Hesske, A. Urakawa, A. Baiker, J. Phys. Chem. C 113 (2009) 12286.
[22] F. Prinetto, G. Ghiotti, I. Nova, L. Lietti, E. Tronconi, P. Forzatti, J. Phys. Chem. B 105 (2001) 12732.
[23] C. Sedlmair, K. Seshan, A. Jentys, J.A. Lercher, J. Catal. 214 (2003) 308.
[24] I. Nova, L. Castoldi, L. Lietti, E. Tronconi, P. Forzatti, F. Prinetto, G. Ghiotti, J. Catal. 222 (2004) 377.
[25] A. Urakawa, N. Maeda, A. Baiker, Angew. Chem. Int. Ed. 47 (2008) 9256.