In situ PM-IRRAS study of powder catalyst: Dynamic evolutions of species on catalyst and in gas phase during NO$_x$ storage-reduction

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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$_2$O$_3$ 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.

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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$_2$O$_3$ 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$_2$O, NH$_3$, H$_2$O, CO, and CO$_2$), and even support materials (e.g. Al$_2$O$_3$ 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$_2$O$_3$ 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.

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2. Experimental

2.1. Catalyst

The Pt-Ba/Al$_2$O$_3$ catalyst (weight ratio: Pt:Ba:Al$_2$O$_3$ = 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$_2$O$_3$ 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}.

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$_2$O, and H$_2$O) 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
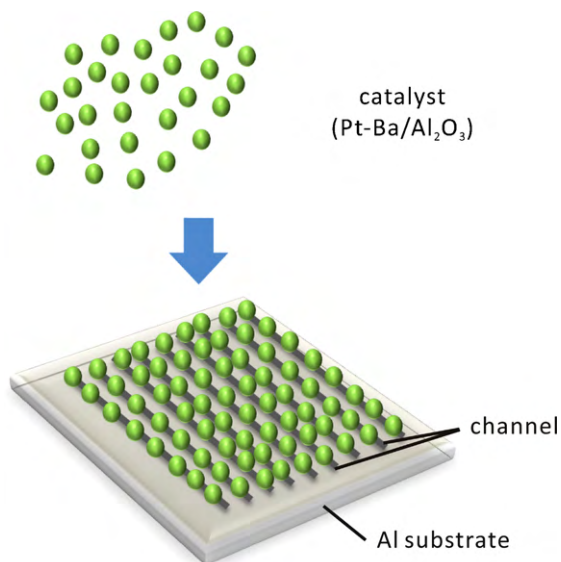

Fig. 1. Schematic drawing of the PM-IRRAS sample prepared by the deposition of catalyst powders into the channels on the aluminum substrate.