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Combining diffuse reflectance infrared spectroscopy (DRIFTS), dispersive EXAFS, and mass spectrometry with high time resolution: Potential, limitations, and application to the study of NO interaction with supported Rh catalysts

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Abstract

We describe a new experiment that combines transmission based structural probes, such as dispersive EXAFS (EDE), with diffuse reflectance infrared spectroscopy (DRIFTS) and mass spectrometry (MS), at high time resolution. The potential and limitations of this experiment are discussed, and an example of its application to the study of fundamental steps occurring during gas–solid interactions is given; that of oxidation and reduction of alumina supported Rh at 573 K using NO and H_2, and the structural-reactive role of linear ($Rh(NO^+)$) Rh-nitrosyl species within these processes.

Keywords: In situ; Time resolved spectroscopies; DRIFTS; Dispersive EXAFS; Mass spectrometry; QSARS; Rhodium; Nanoparticles; γ-Alumina; NO reduction; Selectivity

1. Introduction

The importance of studying gas–solid or gas–liquid processes in situ and with synchronously applied spectroscopies has become more and more evident [1]. Many important processes within catalysis, chemistry, and materials science involve a complex interplay of fundamental physics and chemistry over a wide range of potential parameter space, length, and timescales.

As such, experiments that can combine, without undue sacrifice, two or more complementary spectroscopies are both highly practical and inherently internally consistent. Such experiments have the potential for the derivation of much sought after, though often elusive, quantitative structure function relationships (QSARS) with a high degree of confidence.

Concomitantly, recent years have seen a wide range of experiments that combine techniques implemented. These range from those techniques that operate on widely differing length scales, such as XRD and EXAFS [2,3], to other multitechnique experiments comprising probes of structure, functionality, and reactivity. Experiments permitting processes to be studied using EXAFS in tandem with, UV–vis [4], UV–vis and Raman [5,6], attenuated total reflection (ATR) infrared [7,8], and mass (MS) spectroscopies have been implemented for studying in situ behaviour of working catalysts at both ambient and high pressures and for both gas–solid and liquid–solid systems.

To this burgeoning canon we have recently added a system for synchronously obtaining EXAFS (in transmission), diffuse reflectance infrared spectroscopy (DRIFTS) and MS [9]. The prime driver for this development lay in the wish to be able to address structure, function, and reactivity in gas–solid interactions in a correlated and dynamic manner. It has become abundantly clear that many structural processes, particularly redox cycles in supported metal catalysts that have direct ramifications for catalysts performance, can occur very rapidly indeed [10–18]. Comprehending them, therefore, requires the application of experiments that can probe structure, function,

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and reactivity with sufficient time resolution to be able to capture the processes themselves, rather than just the states that exist before and after they have occurred.

The weak link in this experimental chain has, arguably, been on the structural side of things. For many years extremely rapid reactor based mass spectrometric study of gas–solid interactions has been possible [19]. From a functional perspective, state of the art FT-IR instruments have also been available for some years that are capable of spectral repetition on the few tens of milliseconds time scale (in a single shot) and beyond (in step scan mode for highly reversible processes) [20].

Though it is clear that diffraction based methodologies can now also be achieved on these sorts of timescales it is the case, especially with many homogeneous and heterogeneous catalysts systems, that the reactive phases are not easily amenable to diffraction based study due to their inherent molecular or disordered/small nature. In these cases, what is ideally required is a time resolving elementally specific probe of local structure.

From a practical point of view, this currently means dispersive EXAFS (EDE), wherein a sample is instantaneously illuminated with the energetic bandwidth required to make an X-ray adsorption (XAFS) measurement [21]. Though the Quick EXAFS technology (where an X-ray monochromator is physically moved to scan through the required energy range) that could fulfil the task of recording changes in local structure on such timescales has been developed and demonstrated for both XANES [11] and EXAFS [22] acquisition, to our knowledge there is currently no permanently available and accessible facility dedicated to this end. By contrast there are several dispersive facilities that are currently active with more planned at new third generation facilities currently under construction.

Dispersive EXAFS does, however, come with its own constraints and considerations [21] and, it would be fair to say that, for all the promise of obtaining EXAFS on the timescale of milliseconds in a single shot, it had, until very recently [15,16,18], failed to deliver. There are numerous reasons for this, some of which will be discussed below, but principal amongst these has been the provision of adequate detectors.

As such, in our first demonstration of the current experiment [9] detector readout limitations imposed upon us the collection of dispersive EXAFS and IR data on a timescale of a few seconds. Since then two solutions to this particular problem have arisen: XSTRIP, developed at CLRC Daresbury [23]; and, developed at the ESRF, the Fast Readout Low Noise (FReLoN) detector. With the implementation of this latter detector system for dispersive EXAFS [14] on ID24, restrictions on spectral repetition rates have been essentially eliminated (to the ca. 2 ms level) and we may now use this new experiment in the manner for which it was originally intended.

In this report, therefore, we demonstrate the synchronous application of EDE, DRIFTS, and mass spectrometry to the understanding of a gas–solid interaction on a timescale of a few tens of milliseconds (that of NO and H_2 interacting with Rh supported upon γ-Al_2O_3 at 573 K), and discuss the potential and limitations of this new approach to studying gas–solid processes.

2. Experimental

Synchronous EDE/IR/MS experiments were carried out at the Rh K edge on ID24 at the ESRF using a Si[3 1 1] polychromator mounted in Bragg configuration and utilising a 14 bit ADC FReLoN CCD detector system [14]. Transmission EDE experiments were made synchronously with DRIFTS. The latter were performed at 4 cm^{-1}/64 ms energy/time resolution using a Digilab FTS 7000 spectrometer and a linearized high sensitivity MCT detector. A custom built DRIFTS cell (see below) was used in conjunction with standard (Spectratech) optics. The two techniques could be synchronised to yield sampling rates for each spectroscopy of ca. 64 ms whilst a quadropole mass spectrometer continuously measured the composition of the gas phase. All gases we passed through the cell under mass flow control and, in the case of the He, an inline oxygen/moisture trap (Agilent) was placed prior to the mass flow controller. Gases were switched between cell and bypass using four port microelectric switching valves (Valco).

Five weight percent Rh samples, derived from wet impregnation of $RhCl_3{\cdot}3H_2O$ on γ-Al_2O_3 (Degussa, Alon-C), were synthesised as previously described [9,12–14,16,17]. Ca. 30–40 mg of sieved (90 μm < particle diameter < 120 μm fraction) sample was loaded into the DRIFTS/EDE/MS cell to yield an effective bed density of ca. 0.75 g cm^{-3}. Samples were then purged with He, heated to 573 K under 5% H_2/He (50 ml min^{-1}). They were then briefly reoxidised under 50 ml min^{-1} 5% O_2/He, (to remove any adventitiously adsorbed carbon species) before re-reduction under the 5%H_2/He feed. The appropriate sample temperature was then selected, and the gas flow was briefly switched back to He, before switching to 5% NO/He (50 ml min^{-1}) from a bypass. DRIFTS/EDE/MS data was then collected during between 50 and 120 s of exposure. Reduction of the NO exposed Rh under 5% H_2/He was then monitored through a further switch to He and then to the reductive gas flow (50 ml min^{-1}) whilst, again, the system was constantly monitored using DRIFTS/EDE. Calibration of EDE data was achieved using a room temperature Rh foil. Data reduction and analysis were carried out using PAXAS [24] and EXCURV [25].

2.1. The experiment: design considerations and implementation

One of the prime considerations in designing a multi-technique experiment is that none of the applied techniques are unduly compromised by the experimental geometry that must be adopted to accommodate them. The current case, a fusion of transmission based EDE and DRIFTS, is ideal in this sense: one need not interfere at all with the geometric requirements of either experiment and they can be simultaneously applied in a mutually orthogonal manner.

A schematic of the experimental arrangement is shown in Fig. 1. The overall design philosophy, from a DRIFTS perspective, follows directly from that published by Dr.