# In Situ Structure-Function Studies of Oxide Supported Rhodium Catalysts by Combined Energy Dispersive XAFS and DRIFTS Spectroscopies

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Abstract. The techniques of energy dispersive EXAFS (EDE), diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) and mass spectrometry (MS) have been combined to study the structure and function of an oxide supported metal catalyst, namely 5 wt% Rh/Al<sub>2</sub>O<sub>3</sub>. Using a FreLoN camera as the EDE detector and a rapid-scanning IR spectrometer, experiments could be performed with a repetition rate of 50 ms. The results show that the nature of the rhodium centers is a function of the partial pressures of the reacting gases (CO and NO) and also temperature. This combination of gases oxidizes metallic rhodium particles to Rh(CO)<sub>2</sub> at room temperature. The proportion of the rhodium adopting this site increases as the temperature is raised (up to 450 K). Above that temperature the dicarbonyl decomposes and the metal reclusters. Once this condition is met, catalysis ensues. Gas switching techniques show that at 573 K with NO in excess, the clusters can be oxidized rapidly to afford a linear nitrosyl complex; re-exposure to CO also promotes reclustering and the CO adopts terminal (atop) and bridging (2-fold) sites.

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# INTRODUCTION

Oxide supported metals form a significant proportion of catalytic processes employed in fuels, petrochemicals and environmental protection, as in the Three Way Catalyst (TWC) for automotive exhausts. They form a large class of functional materials that often comprise of distributions of nanoparticulate metals. So it has been appropriate that this has been a substantial field of application for XAFS spectroscopy, with many of these carried out by Lytle [1]. The capability of monitoring the genesis of a metallic catalyst was also recognized, as in a study of Pt/SiO<sub>2</sub> [2]. The potential of XAFS was confirmed by its use in establishing the corrosive chemisorption of small rhodium particles by CO, hitherto used to estimate the surface area of such nanoclusters [3].

Such studies employed scanning XAFS methods and thus were well suited to investigating steady state systems. However, improving the time resolution of spectrum acquisition can not only

improve the productivity of beam time, but also allow kinetic studies and identify reaction transients [4]. The parallel acquisition of the entire spectrum by energy dispersive EXAFS (EDE), which featured in the XAFS-III conference in 1984 [5] was first demonstrated at synchrotron sources in the early 1980s [6], and its ability to probe time dependent phenomena exploited on liquid samples by stopped flow experiments [7] and on dehydration process in a NiY zeolite [8]. More recently, the time resolution and focusing properties of EDE were exploited to provide in situ structural characterization within a flow microreactor of catalyst formation [9] and for structure-function studies of a rhodium catalyst for the reduction of NO [10, 11]. Such studies probe the mean degree of metal aggregation and also the dominant oxidation state of the metal [12]. However, excepting when the metal is substantially dissociated into mononuclear sites, it is difficult to identify the sites adopted by adsorbates.

Infrared spectroscopy, in transmission mode, has been the basis of a well used method of surface site characterization, particularly using CO as the probe molecule [13]. On rhodium, this provided the first evidence for the formation of  $Rh(CO)_2$  surface species [14]. Diffuse reflectance IR spectroscopy is an alternative sample presentation method that avoids the use of disc pressing, which can create voids [15] and modify surfaces and structures [16]. It can also be used for *in situ* studies [17]; when a modulated gas flow was utilized, steady state species could be differentiated from transients, as in a study of CO oxidation catalyzed by Rh/Al<sub>2</sub>O<sub>3</sub> [18].

This study aims at combining all these techniques to probe a sample by XAFS (in its EDE mode), DRIFTS and mass spectrometry so that the local metal environment, adsorbates and gas phase composition may be directly correlated. An outline of this experiment has already appeared [19].

# **INSTRUMENTATION**

The sampling system developed is presented in Fig. 1. The cell is mounted in BN cup within a Spectratech DRIFTS environmental cell modified to provide BN windowing. The IR optical path across an optical bench external to the Digilab FTS7000 spectrometer is perpendicular to the X-ray beamline, and the catalyst is sampled by the IR from above through a single flat CaF<sub>2</sub> or ZnSe window. IR light is focused onto a MCT detector. The entirety can be translated horizontally and/or vertically to locate onto slits, metal foil and a metal-free oxide sample (for focus, calibration and background measurement, respectively). The X-ray beam (100 µm high) is located as close to the top of the sample as will provide a consistent absorption, to maximize the overlap of the region by IR (~0.5mm).



**FIGURE 1.** Sampling arrangement for the DRIFTS-EDE-MS monitoring of heterogeneous catalysis on ID24 (ESRF).

The IR spectrometer was operated in a rapid scanning mode with a 64 ms repetition rate (4 cm<sup>-1</sup> resolution) and the gas phase was analyzed by a Pfeiffer Omnistar quadrupole mass spectrometer in multiple ion monitoring mode.

The longer optimum sample path for transmission at the X-ray energy of the Rh K edge as compared to the L(III) edges of the 5d elements provided a better sampling volume for the IR spectroscopy, typically at the Rh edge the sample was in a 5 mm internal diameter BN cup of 3 mm depth. Scattering effects from windows and sample were also much reduced at the higher energies.

Initially, our in situ measurements using a microreactor cell [10,12] on Beamline ID24 at the ESRF were carried out using a Si(111) monochromator in a Laue geometry detector and a Princeton CCD camera. The former was replaced by a Si(311) monochromator in a Bragg geometry which provided a stable source, good spectroscopic resolution and a larger focal spot in the horizontal plane (500 µm) that can be accommodated by the DRIFTS cell. The read-out time of the CCD camera  $(\sim 0.3 \text{ s for a single set of binned stripes})$  meant that the EDE detection could not match the timescale of the IR spectrometer, but replacing this by a FreLoN camera [20] resolved this problem. These modifications [21] allowed the two spectroscopies to be operated synchronously with the same repetition rate.

The temperature of the sample is set by a Eurotherm controller and the gas environment by switching valves and mass flow controllers, with flow patterns that can be modulated by a wave form generator.

Data reduction was carried out using PAXAS [22], with EXAFS analyzed by EXCURV98 [23] and XANES via FEFF8 [24].

# CATALYST PREPARATION

5wt% Rh samples, derived from wet impregnation of RhCl<sub>3</sub>.3H<sub>2</sub>O on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Degussa, Alon-C), were synthesized as previously described [10, 12]. Ca. 30-40mg of sieved (90 µm <particle diameter< 120µm fraction) sample, was loaded into the DRIFTS/EDE/MS cell to yield an effective bed density of ca. 0.75 gcm<sup>-3</sup>. Samples were then purged with He and heated to 573 K under 5% H<sub>2</sub>He (50 mlmin<sup>-1</sup>) to effect re-reduction of the supported rhodium.

## RESULTS

## **Instrumentation Characteristics**

The sampling arrangement proved to be effective at Rh and Pd K-edges. With the FreLoN camera, a typical acquisition time for a single frame was ~ 2.5 ms. Time resolved experiments were based upon ~ 25 acquisitions giving an effective repetition rate of 50 - 60 ms. On the 5 wt% catalysts this provided acceptable XANES and EXAFS features to ~ 12 - 14 Å<sup>-1</sup> [25]. For 2 wt% samples, this repetition rate afforded poorer EXAFS data ( $k_{max} \sim 9 - 12 \text{ Å}^{-1}$ ) which generally could only sustain a single shell fit. In isothermal experiments following gas switching, reactions were monitored over a period of 40 – 90 seconds.

#### **Nature of the Rhodium Catalysts**

The structural distribution of the Rh/Al<sub>2</sub>O<sub>3</sub> catalysts was investigated by a combination of techniques including TEM, EDX, XPS, and Rh and Cl K-edge XAFS [26]. TEM shows a distribution peaking at 20 Å diameter. However, it has been established that such particles are rapidly oxidized by O<sub>2</sub> [12] so the rhodium particles sampled would have been expanded by aerial oxidation prior to introduction to these measuring technique. Rereduction by 5% H<sub>2</sub>/He rapidly regenerates metallic structures as evidenced by in situ Rh K-edge XAFS [12]. A first shell Rh-Rh coordination number of ~ 7 is normally derived for such catalysts, corresponding to a mean particle size of ~ 40 atoms [27]. XANES calculations using FEFF8 [24] were carried out on model clusters from Rh<sub>3</sub> to Rh<sub>87</sub>. The observed features converged by Rh<sub>55</sub> but up to that point provided sensitivity to the particle size [27]. These 5wt% Rh/Al<sub>2</sub>O<sub>3</sub> samples afforded spectral features most closely matched by the Rh<sub>43</sub> model, consistent with the results of EXAFS analysis.

#### Reaction of Rh/Al<sub>2</sub>O<sub>3</sub> with CO and NO

#### Temperature Ramped in Situ DRIFTS-EDE-MS

The range of structural changes was scanned by a temperature ramp experiment (Fig. 2) with one spectrum recorded every 1°. Variations in the XAFS show structural changes leading to metallic particles being created at the higher temperatures. Simultaneously, the DRIFTS spectra showed changes in the adsorbates on the rhodium sites. The IR spectra in the region shown in Fig. 3 are dominated by the two bands of the *gem*-Rh(CO)<sub>2</sub>

unit, their relative intensities suggesting a OC-Rh-CO bond angle of slightly greater than 90° [28]; the bands below 1800 cm<sup>-1</sup> are attributable to NO derived species in a bridging or a bent Rh-N-O geometry [29]. As the intensity of the carbonyl bands begin to decrease (~ 450 K), a new nitrosyl band due to a linear Rh-N-O structure grows in. Modeling of the XANES and EXAFS patterns of materials where this is the predominant IR active species (573 K under 5% NO/He) suggested that rhodium may coexist as oxidized nitrosyl centers and fcc nanoparticles. It is above the temperature at which the intensity of the Rh(CO)<sub>2</sub> IR bands reach their maximum that the rate of conversion of NO to N<sub>2</sub> and N<sub>2</sub>O begins to increase, and the mean Rh-Rh coordination number increases from  $\sim 2$  to  $\sim 3$ . Above 560 K, the coordination number increases more rapidly, reaching a value of ~5.5 at 573 K; this accompanies the loss of the  $Rh(CO)_2$  units and a rise in the catalytic reduction of NO. It appears that the dicarbonyl acts as a precursor to the active catalyst species, as observed for CO oxidation by  $O_2$  [12].



**FIGURE 2.** Selected Rh K-edge XAFS of 5 wt%  $Rh/Al_2O_3$  (ex RhCl<sub>3</sub>) in the DRIFTS-EDE-MS cell under 2.5% NO: 2.5% CO: 95% He during a temperature ramp from 300 - 573 K at 10 K/min.

#### Isothermal in Situ DRIFTS-EDE-MS Studies

In order to probe the structural changes more directly, isothermal experiments were carried out at

three temperatures: 473 K, at the onset of catalysis, a temperature above the rise in Rh-Rh coordination



**FIGURE 3.** Selected DRIFTS spectra of 5 wt% Rh/Al<sub>2</sub>O<sub>3</sub> (ex RhCl<sub>3</sub>) in the DRIFTS-EDE-MS cell under 2.5% NO: 2.5% CO: 95% He during a temperature ramp from 300 - 573 K at 10K/min.

number (573 K) in line with the catalysis and a temperature at which catalysis proceeds rapidly (623 K). The pre-reduced catalyst was held under 5% CO/He and then the gas was switched to 5% NO/He; after 10 s the gas was switched back to CO/He; this sequence was repeated several times.

The variations in coordination number at 473 K are small, being between 4 and 5. Any variation that might be statistically significant did not follow the cycle of the gas switching. The concomitant IR studies showed that the cycle commenced with the Rh(CO)<sub>2</sub> as the main component and this was converted into the oxidized linear Rh-NO species within the 10 s exposure to NO/He. Reversion to the dicarbonyl occurred following re-exposure with CO/He. Since both of these sites have oxygens as auxiliary ligands, it would not be expected that this interchange would have an influence on the Rh-Rh coordination number.

However, at 573 K the variations in Rh-Rh coordination number are substantial. Once the pattern is established after 30 s, introduction of NO reduces  $N_1$ (Rh-Rh) to ~2.5, and addition of CO returned it to a value of ~6. This might be correlated with mean nuclearity variations between ~4 to ~20 [27], but may well be due to the degree of oxidation of the metallic particles [26]. Again, the IR spectra

also track the cycles closely, but at this temperature there are no bands attributable to the  $Rh(CO)_2$  unit. Instead, the two v(CO) peaks observed are due to terminal (atop) and bridging (two-fold) sites, as adopted on metallic rhodium [14]. Hence in this cycle, both structural techniques demonstrate an inter-conversion between oxidized and metallic rhodium centers as the gas composition is changed. At 623 K the pattern of behavior is similar. Exposure to NO reduces the value of  $N_1$ (Rh-Rh) to ~5.5 and exposure to CO increases the value to ~8, corresponding to mean variations in the mean metallic core of between ~15 and ~70 atoms. The IR behavior is similar to that found at 573 K, excepting that the bridging CO band is weaker in intensity. At both of the higher temperatures, the rate of variation of the IR spectra is faster than the cycle of gas changes.



**FIGURE 4.**  $N_1$ (Rh-Rh) values from analysis of EDE spectra of 5 wt% Rh/Al<sub>2</sub>O<sub>3</sub> (ex RhCl<sub>3</sub>) in the DRIFTS-EDE-MS cell initially under 5% CO: 95% He. Switch to 5% NO: 95% He at 0, 20, 40, 60 and 80 s; reversion to CO/He was at 10, 30, 50, 70 and 90 s. T = 473 K (middle – low amplitude), 573 K (bottom), 623 K (top).

# CONCLUSIONS

These experiments demonstrate the viability of combining X-ray and infrared spectroscopies in a time resolved manner. The timescales of the measurements are faster than the dead time of the gas mixing ( $\sim 2$  s) and thus are not the limiting factor in kinetic study. Being able to carry out all techniques in a parallel mode greatly assists studies on these timescales. Taking the NO/CO reaction as an exemplar, these studies provide far more detail about the inter-relationships between catalyst structure and activity. As in previous studies on NO reduction by

 $H_2$  [10] and CO oxidation by  $O_2$  [12], temperature and partial pressure of the reactant gases both influence the majority structure adopted by the active metal. By adding the combination of techniques to the gas-switching, it can now be seen that these catalyst inter-conversions are fast under operating conditions. There are substantial structural changes required to convert an isolated Rh-NO site into a cluster of metal atoms that can sustain bridging as well as terminal CO groups; these are rapid processes and no other transients could be observed.

In principle these techniques can be developed in two further ways. First, the small dimensions of the focal spot of the dispersive XAFS experiment could be exploited to provide a cell with a much smaller dead-time, thus improving the time resolution up to or beyond that attainable with the FreLoN detector (2 ms). Higher time resolutions have already been demonstrated with a microstrip detector [30]. Secondly, an anisotropic DRIFTS sample cup could optimize both the IR and XAFS requirements or transmission geometry could be adopted for the IR measurements.

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