Behavior of Rh catalysts during NO reduction by CO with time resolved EXAFS and FTIR

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Introduction

As one of the components of the Three Way (automotive exhaust) Catalyst (TWC), oxide supported rhodium has some significance. Probing the surface properties by CO absorption has produced some debating points, with a key observation on alumina supported rhodium being that IR spectroscopy revealed $Rh(CO)_2$ units as well as bands attributed to terminal $(Rh-\eta^1-CO)$ and bridging (μ) CO sites [1]. X-ray absorption spectroscopy provided structural insight about the site of the $Rh(CO)_2$ units, showing that, rather than being part of the metallic particles themselves (for example of edge sites of rafts), these units were isolated Rh(I) centers coordinated to surface oxides [2]. This corrosive chemisorption has been studied more recently by energy dispersive EXAFS (EDE) [3]. This same species has also been observed during the catalysis of another of the TWC processes, CO oxidation to CO_2, by Rh/Al_2O_3, with its occurrence being closely related to the partial pressures of the two gases and also the temperature [4]. Catalysis occurs more readily though under more oxygen rich gas mixtures when Rh(III) centres predominate. In contrast, the reduction of NO by H_2, modelling the reduction of NO by unspent fuel, was found (by in situ EDE) to proceed to afford N_2 only when small metal particles were the predominant state of rhodium [5].

The third TWC reaction is the redox reaction between NO and CO, which ideally should have high selectivity to CO_2 and N_2, and not to the less environmentally benign N_2O. Both of these gases provide strong intense chromophores in the infrared when they are adsorbed onto transition element sites, and the frequency of these vibrations is sensitive to the nature of the binding mode and also to the oxidation state of the metal involved. So, in principle the combination of X-ray absorption fine structure (XAFS) and infrared spectroscopy can provide complementary information about the nature of the metal sites as they are affected by ambient gases, including situations under catalytic conditions. Then more direct structure-reactivity correlations may be derived.

Methods and Materials

A sampling system based upon a commercial (Spectratech) diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) in situ cell (with CaF_2 or ZnSe as IR windows) was constructed using BN as the sample cup and also the window material in the X-ray path [6]. The cell was mounted on an external optical bench of a Digilab FTS7000 IR spectrometer with a high sensitivity MCT IR detector. The IR optical path is perpendicular to the X-ray path as provided by the energy dispersive EXAFS Beamline ID24 at the ESRF. The external bench was fixed to the spectrometer and the whole could be translated horizontally between sample and reference positions.

Using a FReLoN camera as the EDE detector repetition rate for both IR and EDE could be maintained at ~ 60 ms. A Si(311) polychromator in a Bragg geometry was employed. Energy calibration was against the spectrum of a rhodium foil. Background subtraction utilized the program PAXAS [7] and data analysis via EXCURV98 [8] and FEFF8.2 [9].

The ambient gases were based upon 5% mixtures in He and can be switched under computer control; gas compositions were monitored by a Pfeiffer quadrupole mass spectrometer.

The Rh/Al_2O_3 was prepared by wet impregnation from rhodium (III) chloride onto Degussa Alon C, calcined, sieved to ~100 μm particle size and reduced at 573 K by hydrogen [5].

Results

The instrumentation used is presented in Fig.1. The view is along the X-ray beamline showing the DRIFTS cell encapsulated by the IR collecting mirror, the focussing mirror and the MCT detector. At the energies of the Rh and Pd K-edges, the sample cups used were 5 mm internal diameter and this allowed the acquisition of good X-ray absorption spectra while also providing an appropriate sampling area for the DRIFTS measurements.
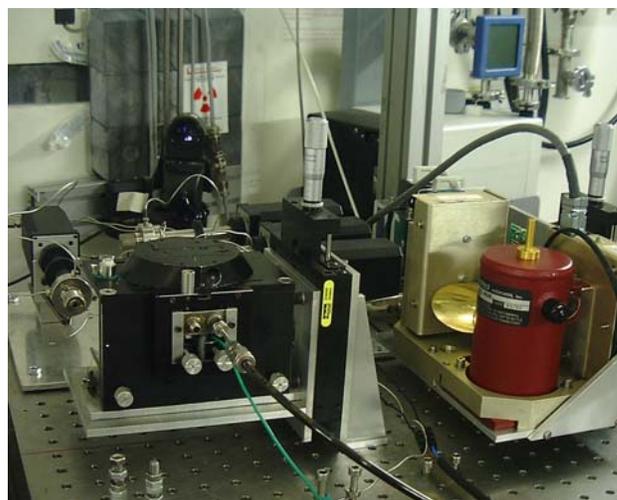
Fig. 1. DRIFTS-EDE cell mounted on beamline ID24 showing the IR optical and detector system.

The samples in question were of 5 wt% Rh/Al_2O_3 and direct transfer into a cell with exposure to air results in oxidation, as evidenced by the Rh K-edge XAFS spectrum [4]. However this can be recovered by in situ reduction with 5% H_2/He. The particles so obtained from a rhodium(III) chloride precursor

afford a Rh-Rh coordination number of ~ 7.3(6), corresponding to a mean particle nuclearity of 40-50 atoms [10]; simulation of the XANES features by fragments of *fcc* structures is also consistent with this proposal. In the absence of oxygen, such particles are only very partially dispersed by exposure to 5% CO/He for 36 s. The DRIFTS spectra in the ν(CO) region indicate a mixture of the terminal (2060 cm^{-1}) and bridging (1908 cm^{-1}) sites on metallic rhodium in addition to some of the isolated $Rh(CO)_2$ units (2099 and 2037 cm^{-1}). Exposure to NO/He, however, causes a very rapid, exothermic oxidative disruption of the Rh particles [11].

Under the catalytic gas mixture (2.5%CO: 2.5% NO/He) there is also rapid reduction in the mean Rh-Rh coordination number (to ~ 3.3) and the accompanying IR spectra are dominated by the $Rh(CO)_2$ unit. As the temperature is raised, the intensity of these bands increase and reach a maximum at 450 K, at which point the mean Rh-Rh coordination number has dropped to ~ 2.3. The onset of catalysis ensues above this temperature. At higher temperatures (525 – 550 K), the absorption band of a linear nitrosyl (~ 1920 cm^{-1}) dominates the IR spectrum in this region. At 550K the Rh-Rh coordination number begins to increase from 3.5 to 5.5 at 575K, at which temperature the nitrosyl band is decreasing in intensity.
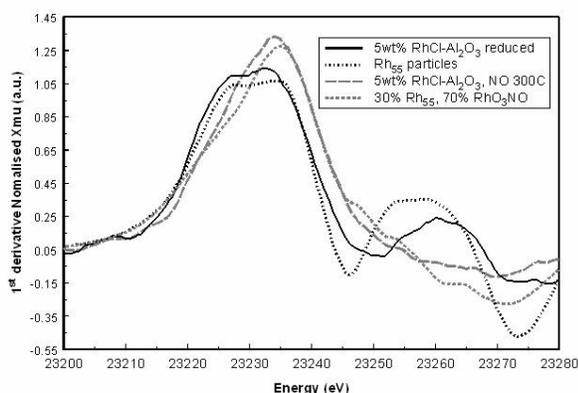
Fig. 2 Simulation of the first drivative of the XANES features of 5% Rh/Al_2O_3 and after exposure to 5 % NO/He at 573K.

It appears that at higher temperatures, there is a linear nitrosyl species that co-exists with metallic particles, and this is evident both under NO and the NO/CO mixture. At 573 K under 5% NO/He, the Rh K-edge EXAFS can be fitted by a linear Rh-N-O unit and also ~2.7 Rh-Rh bonds. Fig. 2 shows a simulation of the XANES features. Consistent with the IR and EXAFS analysis, this can be accommodated by a mixture of *fcc* particles and an oxidised Rh-NO site with oxides groups forming the rest of the coordination sphere.

To probe the kinetics of structural change, a gas switching regime was established at constant temperature, with CO and NO alternated every 10 seconds. At 473 K (Fig. 3) there is little change in the Rh-Rh coordination number with gas switching, as may be expected when the predominant species in the $Rh(CO)_2$ unit under CO. At the higher temperatures, the changes are more substantial and follow the course of the gas switching more closely. The IR spectra show that the Rh-NO forms under NO and after the gas switch, the spectrum changes to that of CO on metallic rhodium.

Discussion

These results show that time resolved studies by appropriate combinations of characterisation techniques can provide a considerable depth of information about the nature of catalytic materials. It is evident that significant structural changes occur for Rh/A_2O_3, from their pre-preparation in situ through exposure to the reacting gases and during the temperature ramp to operating conditions. All of these changes in condition are within those of the cycle of operation of the Three Way Catalyst.
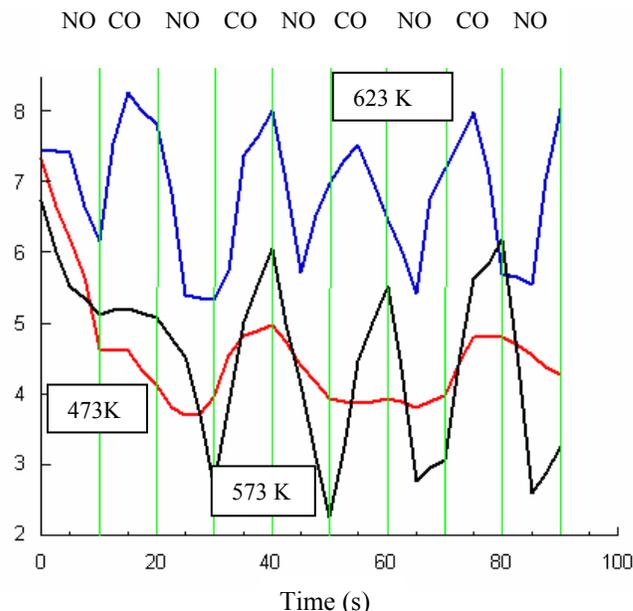
Fig 3. Variation of Rh-Rh coordination during the NO/CO switching over 5wt% Rh/Al_2O_3 at; 473 K, 573 K and 623 K.

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