



	Experiment title: Real time mapping of active phase gradients within working catalyst beds using Dispersive EXAFS.	Experiment number: CH-1469
Beamline: ID24	Date of experiment: from: 5 th March 2003 to: 11 th March 2003	Date of report: 6 th August 2003
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Report: The aim of this proposal was for the first time to make use of the considerable spatial resolution afforded by Energy dispersive EXAFS (EDE), in tandem with its well known temporal resolution, to study the axial structural variance of working catalysts along a catalyst bed. The absence or presence of such structural gradients is of considerable interest in the realistic application of heterogeneous catalysts and is not easily established in any other way. The beamtime allocation was entirely successful in this respect but also proved fruitful in other areas: not least of which is the demonstration of EDE as a powerful and unique tool for the rapid assessment of a wide range of parameter space that may be used to define a working catalyst.

Experiments at ID24 were carried out at the Rh K edge using the unique Laue polychromator facility developed at the ESRF and a peltier cooled CCD detector, in tandem with a custom made microreactor designed and built in Southampton. 20 mg sample was loaded into the microreactor to form a 5mm long packed powder bed through which gas mixtures were passed. This arrangement is unique in that it permits EDE interrogation of the working catalysts under conditions of plug flow, wherein the superficial contact time (of the gas with the catalyst) may be well defined and accurate temperature measurement ensured through the insertion of a thermocouple directly into the catalyst bed. The catalytic reactivity and selectivity of the reactions under investigation were constantly monitored using the mass spectrometer available at ID24.

Catalyst-bed mapping experiments were made by stepping the sample bed position horizontally at 200 μm intervals from the gas inlet to gas exhaust ends of the bed and collecting an EDE spectrum at each point. Once complete the temperature of the sample was increased by 25K and the procedure repeated to build up a picture of how the structure of the Rh phase varied axially along the catalyst bed during CO oxidation and NO reduction by H₂ as a function of both temperature and composition.

Figures 1a-c shows some results of this approach for CO oxidation. From these data three highly significant observations are made. The first is that no major gradients in Rh structure (from EXAFS) exist during operation under the conditions indicated despite the fact that at high conversion considerable variation in gas phase composition is occurring from the inlet to the exhaust end of the catalysts bed. However, significant gradients in the near edge structure are observed (see especially 1c). These variations in XANES structure are indicative of small variations in the level of Rh oxidation occurring along the bed and indicate that at high conversions all the activity resides in the first 1-2mm of the bed.

The second observation is that even the relatively simple CO oxidation reaction over highly dispersed Rh is extremely structure sensitive, with the Rh phase varying greatly as a function of temperature and gas phase composition. This observation flies in the face of much conventional wisdom (derived from low dispersion single crystal and foil models of such catalysts) regarding the manner in which this conversion is achieved over Rh catalysts.

Conventional models consider that Rh metal surfaces provide the active sites for this and other reactions, and that the surface chemistry of adsorbed CO and O dictates how the catalysis proceeds. Our results show that this is true over only a very small proportion of the feedstock composition/temperature parameter space that such systems may operate under (figure 1 b).

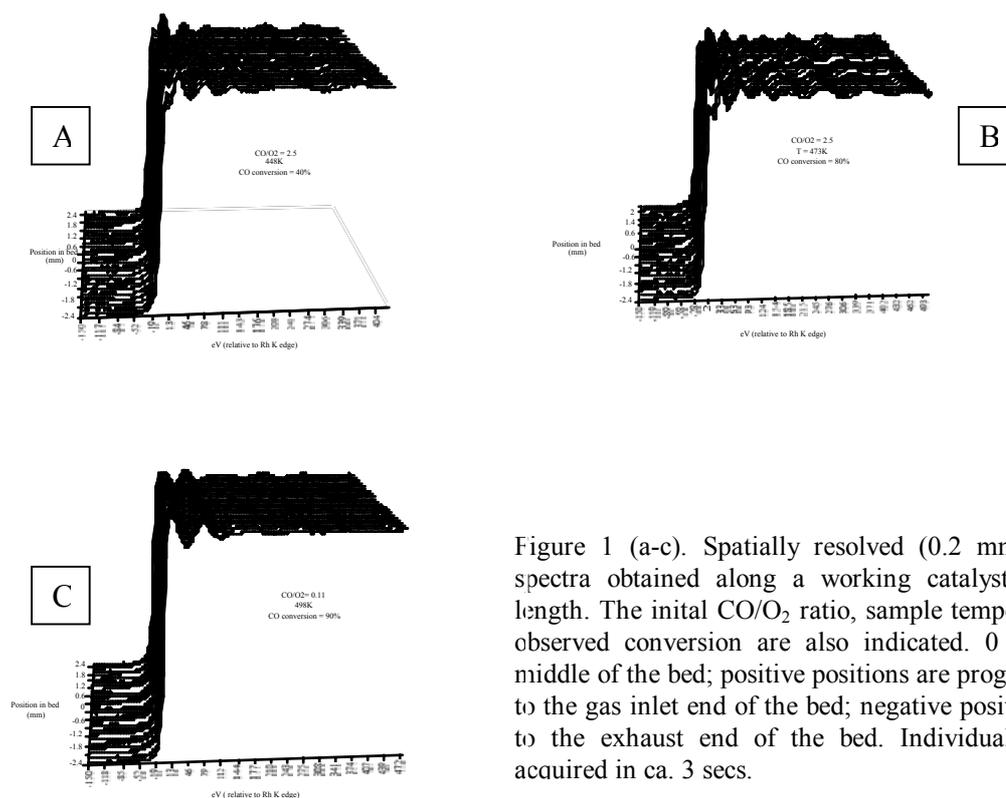


Figure 1 (a-c). Spatially resolved (0.2 mm steps.) EDE spectra obtained along a working catalyst bed 5mm in length. The initial CO/O₂ ratio, sample temperature and net observed conversion are also indicated. 0 represents the middle of the bed; positive positions are progressively closer to the gas inlet end of the bed; negative positions are closer to the exhaust end of the bed. Individual spectra were acquired in ca. 3 secs.

Over most of this parameter space, and in the most commercially relevant regimes of low CO/O₂ fractions, the active phase throughout the bed is a defective nanoparticulate Rh oxide. Moreover, in terms of reaction “light off” this phase is more efficient than the metallic form of Rh produced at higher temperature under reducing (high CO fraction) conditions (not shown). Such a kinetic variation (as a function of CO fraction) is expected from low dispersion models of this reaction occurring over extended Rh surface. Again, however, our spatio-temporal approach to probing the dynamics of active phase change shows that the reasons for this are much more complicated than these models would have us believe. By drawing upon previous results we have derived on ID24 regarding related systems (M A Newton et al J. Phys. Chem A, 2001, 105, 5965 and J. Phys. Chem B, 2002, 106, 4214) we can show that the state of Rh indicated by figure 1a is one of a nanoparticulate Rh co-existing with ca. 50% Rh(CO)₂. A full expression of the catalytic capacity of the system under these conditions is not achieved until this latter species becomes thermally unstable to the degree that metallic Rh becomes the dominant surface phase.

In addition to these highly significant results during these “bed mapping” experiments the occurrence of complex and autonomous oscillatory behaviour in CO oxidation (but not NO reduction by H₂) was observed. Such oscillatory behaviour has been observed for this reaction over Rh catalysts before, however, our approach has allowed us, for the first time, to probe the structural variations occurring in the active phase during this behaviour. These data, and its implications, are still being analysed. Lastly, this time was also used to investigate the dynamic response of nanoscale Rh catalysts to H₂S and SO₂ and the effect this has on NO reduction by H₂. These experiments have highlighted the very rapid, but very different responses that Rh nanoparticles have to these sulphur containing molecules and has already been published (see below).

In summary we have demonstrated that the unique spatio-temporal properties of EDE, in tandem with a plug flow microreactor, can provide an unparalleled means to rapidly investigate the structural-reactive behaviour of catalysts working under realistic conditions, and to gain new and fundamental information regarding how these systems work.

Papers published arising from this beamtime allocation:

“Contrasting dynamic responses of supported Rh nanoparticles to H₂S and SO₂ and subsequent poisoning of NO reduction by H₂” M A Newton, A J Dent, S Diaz-Moreno, S G Fiddy, B Jyoti, and John Evans, *Chem. Comm.*, **2003**, 1906.

Papers in submission or preparation arising from this beamtime allocation:

“Rapid spatial and temporal assessment of the nature and interconversion of supported catalyst phases and their influence upon performance: CO oxidation to CO₂ by Al₂O₃ supported Rh catalysts”. M. A. Newton, A. J. Dent, S. Diaz-Moreno, S. G. Fiddy, B. Jyoti, and J. Evans. *Submitted to J. Am. Chem. Soc.*

“On the source of autonomous oscillatory behaviour during CO oxidation by supported Rh catalysts.” M. A. Newton, A. J. Dent, S. Diaz-Moreno, S. G. Fiddy, B. Jyoti, and J. Evans. *In preparation*