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INDUSTRIAL APPLICATIONS OF EXAFS/XANES

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Abstract

Direct industrial application of x-ray absorption spectroscopy is demonstrated by research in catalysis (CO/H₂ and naphtha reforming) and corrosion protection.

1 Introduction

X-ray absorption spectroscopy (XAS) has rapidly become the major technique associated with real industrial synchrotron applications. This stems from the very particular advantages offered. Structural information can be derived in a wide range of non-crystalline situations including wet materials or solutions and it is a resonance technique so that a specific kind of atom centre can be investigated. Using fairly hard x-rays material is accessible at interfaces, in pores or in realistic sample environments. Finally the technique can be made surface/interface specific under conditions for total reflection. These points are illustrated by examples drawn from CO/H₂ and naphtha reforming catalysis and corrosion protection carried out experimentally at Daresbury SRS.

2 Porous Oxide Supported Rhodium Catalysts

It has been shown that selectivity in the conversion of CO/H₂ to ethanol depends markedly on catalyst preparation procedures [1] and in particular on the rhodium precursor. The existence of small particles on very porous and sometimes heavy supports prevented techniques such as XPS and TEM from giving a complete structural picture. Fig 1 shows Rh K edge EXAFS for rhodium foil and a series of such catalysts following reduction in situ in flowing H₂ at 300°C in a treatment rig [2]. For 1%Rh on SiO₂ measurements were carried out in transmission but for heavy oxide supports (WO₃) the rig has been modified to allow fluorescence detection.

Table 1 lists the first shell co-ordination numbers and bond radii derived from the EXAFS by curve fitting using the spherical wave scattering model contained in the program EXCURVE at Daresbury [3]. In this program calculated phase shifts are refined against standard materials. Also shown in table 1 are Rh crystallite sizes estimated from the co-ordination numbers using published calculations for ideal cuboctahedral crystals [4].
The size information correlates nicely with changes in selectivity. In order to understand more fully the differences in fig 1 data for Rh foil was first examined in detail. Fig 2a shows the computer fit for four shells of the structure using standard crystallographic data. The fit is good but the splitting at 10.2Å⁻¹(395 ev) is not reproduced and comparison

![Fig 1 Rh K edge EXAFS (filtered)](image)

![Fig 2 Comparison of experimental (-) and theoretical (---) k³ EXAFS](image)

of the fourier transforms indicates that the fourth shell contribution is substantially underestimated. Fig 2b shows the fit including the multiple scattering term due to the linear configuration involving the central atom, first shell and fourth shell and demonstrates that the feature at 10.2Å⁻¹ provides a guide to the growth of crystallites in terms of the fraction of atoms which have a complete ordered fcc environment. Catalysts can therefore be quickly differentiated. We have not yet completed multishell modelling for the catalysts but the fourier transforms show the development of higher shells with size and confirms the importance of crystallite size and surface geometry in controlling catalyst selectivity.

### TABLE 1

EXAFS results for reduced oxide supported 1% Rh catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rh-Rh (Å)</th>
<th>2σ²(Å²)*</th>
<th>Crystallite diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh Foil</td>
<td>2.69</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>Rh(NO₃)₃/SiO₂</td>
<td>2.69</td>
<td>0.012</td>
<td>20</td>
</tr>
<tr>
<td>Rh₂O₃/SiO₂</td>
<td>2.69</td>
<td>0.011</td>
<td>70</td>
</tr>
<tr>
<td>RhCl₃/SiO₂</td>
<td>2.70</td>
<td>0.008</td>
<td>&gt;100</td>
</tr>
<tr>
<td>RhCl₃/WO₃</td>
<td>2.69</td>
<td>0.009⁺</td>
<td>30</td>
</tr>
</tbody>
</table>

* 2σ² is a Debye-Waller factor including static and thermal disorder.

⁺Cooled with liquid N₂. Otherwise all measurements at room temperature.
This in turn depends on precursor and support. We have seen no evidence for support/metal interactions [5] but this is not surprising since even for 20Å particles it is estimated that as few as 4% of the bonds could involve oxygen.

3 Alumina Supported Pt/Re Naphtha Reforming Catalysts

The preparation of reforming catalysts involves a number of classic but poorly understood basic steps such as impregnation, calcination and reduction followed by modifying steps such as sulphiding. This paper concentrates on sulphiding because it illustrates the importance of XAS as a resonance technique. An important part of the work too has been the use of edge data for interpretation. Fig 3 shows Pt L₃ edges for different oxidation states. At the edge absorption occurs via a fully allowed pseudo-atomic transition, 2p→5d, with intensity depending on the number of unoccupied valence levels [a]. There is an excellent correlation between the normalised white line amplitude and oxidation state. A similar correlation exists for ReL₃.

![Fig 3 Pt L₃ edge XAS (displaced for clarity) for some standard materials showing the correlation between normalised white line intensity (Aₑ/Aₚₚ) and oxidation state

(a) Pt foil (b) PtCl₂ (c) PtO₂.2H₂O (d) Na₂Pt(OH)₆ (e) H₂PtCl₆ (f) PtS](image)

Fig 4 shows Pt and Re L₃ XAS data for 2.5% Pt and Re on Condea Al₂O₃ for two sulphiding procedures giving widely different catalyst performance. Using the edge data (fig 4) with the fourier transforms (fig 5) and detailed computer fitting shows that poor performance is associated with complete conversion of Pt to PtS (4S atoms at 2.31Å) while Re is not sulphided at all. The revised sulphiding procedure gives partial conversion of both Pt and Re with PtS (50%) forming a coating on Pt preventing air oxidation while Re is clearly not protected in this way. Under in situ reduction conditions at 450°C PtS is completely reduced to Pt fcc crystallites while Re S₂ remains. Detailed computer fitting (fig 6) gives 42% ReS₂/58% Re.

![Fig 4 Pt and Re L₃ XAS for 2.5% Pt/2.5% Re on alumina

(a) original sulphiding procedure followed by air exposure
(b) revised procedure and air exposure
(c) (b) reduced in H₂ at 450°C](image)

11.2 11.6 12.0 10.2 10.6 11.0 KeV
Fig 5 $k^3$ weighted fourier transforms without phase shifts for 2.5% Pt/2.5% Re on alumina

(a), (b) original sulphiding procedure followed by air exposure

(c) revised procedure and air exposed

(d) (c) reduced in $H_2$ at 450°C

Fig 6 Computer fit to the filtered Re $L_3$ EXAFS for reduced sulphided catalyst (expt -, theory ---) giving average co-ordination numbers of 2.5S atoms at 2.30Å and 7.1 Re at 2.74Å i.e. 42% octahedral ReS$_2$ with 58% Re.

4 Surface Coatings and 2 Dimensional X-ray Techniques

Coatings for corrosion protection or adhesives can readily be tested by conventional salt spray or mechanical tests. Information on the interfacial chemistry responsible for the important barrier or adhesion properties is less easily derived. Fluorescence EXAFS provides an opportunity to look at interfaces non-destructively in situ. To test this thin layers of metals (7-100nm) were deposited on glass and coated. Thicknesses of metals were chosen so that the entire layer was consumed during the ensuing interfacial reaction. Fig 7 shows results for 'Haloflex', an ICI water based vinyl chloride/vinylidene dichloride polymer emulsion with impressive corrosion protection properties. All the original Fe reacts and the reaction product depends on coating pH. Comparison of the XANES region to define pre-edge features and edge position (fig 7) with a series of Fe (II) and Fe (III) compounds and data in reference [6] gives Fe (II) at pH 2 and Fe (III) at pH 4.5 with a separation of 3eV. The pre-edge spectrum, EXAFS, fourier transforms and computer fitting indicate octahedral first shell co-ordination with 40 at 2.16Å plus 2Cl at 2.61Å and 60 at 2.09Å respectively approximating to the environment round Fe in FeCl$_2$$\cdot$4H$_2$O and Fe (III) oxide systems.
Fig 7  Fe K edge XAS, edge spectra and fourier transforms (without phase shifts) for (a) 60µm 'Haloflex' at pH2 on 300Å Fe supported on glass (b) pH 4.5 coating (c) 300Å Fe on glass

The above research has relied on carefully controlled thicknesses of metal films. However by working at the appropriate critical angle of incidence X-rays will totally reflect at an interface. The resultant reflected (REFLEXAFS), scattered and fluorescence (FREXAFS) beams all contain structural information about the interfacial region [7]. These techniques are being developed jointly with the University of Strathclyde to examine solid/solid and liquid/solid interfaces of importance to the chemical industry, for example, corrosion protection.

So far we have been able to detect the oxide films on Fe, Ag and Cu, thus confirming surface specificity, and a metal surface under liquid and its subsequent modification following chemical reaction. This is illustrated by the formation of silver sulphide on Ag under saturated aqueous H$_2$S [8].

References

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4  P Chini, Gazzetta Chimica Italiana 109, 225 (1979)