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X-RAY EMISSION SPECTROSCOPY OF INDUSTRIAL CATALYSTS IN THE STEM

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Résumé - On présente des mesures réalisées sur des catalyseurs montrant certaines des limitations de l'analyse par émission X dans le STEM. Ces limitations sont dues à la dégradation de l'échantillon et à la taille du faisceau. Le taux de comptage est comparé aux valeurs théoriques pour des tailles de sonde limitées par l'aberration sphérique. Une bonne corrélation est trouvée pour les particules de taille comprise entre 1 et 25 nm.

Abstract - Examples of limitations to XES analysis of catalyst specimens in the STEM due to specimen degradation and probe size are presented. Absolute count rates as a function of particle size are compared with theoretical values for spherical aberration limited probes. Good agreement with the predicted size dependance is found in the range 1 to 25 nm.

A major advantage of the STEM for the characterization of materials by X-ray emission spectroscopy is the ability to form a very small probe of high intensity. This has given rise to many applications in the chemical analysis of particles from a few nanometers to several microns in diameter /1,2/. In this paper, examples are taken from the field of heterogeneous catalysts, consisting typically of light oxide carriers such as alumina or zeolites supporting heavy metal (Pt, Pd...) or alloy particles 1 to 50 nm in diameter. Typical applications to these systems are well documented /3,4/. We will consider here two examples showing the effects of damage to the specimen and of the spatial distribution of electrons in the probe.

Some of the most beam sensitive materials in this field are in the zeolite family of supports. The example given in Figure 1 shows a crystal of an L-zeolite industrial preparation. This zeolite contains potassium. Of interest here is the relative concentration of Al, Si and K as a function of distance from the centre. Figure 1 (a) shows the particle after analysis at five points, at the mid point of each edge and at the centre.

Severe structural damage is evident at the edges after 100 seconds. A potassium X-ray map (Fig. 1 (b)) shows that chemical changes have also been induced, the areas analysed are now potassium deficient. No evidence of aluminium or silicon depletion was found however and the resulting Al/Si ratios agree with previous work in that the particle is silicon rich at the centre. Figure 1 (c) shows two spectra from opposite edges indicating the consistency of such analyses whilst Figure 1 (d) compares a spectrum taken at the edge with one from the centre. In the latter the signal is generated throughout the depth of the particle but the enrichment in silicon is evident. Figure 1 (e) shows the results of analysis of the nearby holey carbon support film before and after examination of the crystal. The potassium appears to be "sputtered" off the particle onto the film by the electron beam, rendering measurement of the distribution of this element impossible in this case.

Fig. 1 - (a) Zeolite pellet after analyses of 100 seconds at the mid point of each edge and at centre ; (b) potassium distribution map corresponding to (a) ; (c) a spectrum from the edge (in white) compared with that from the centre (black) ; (d) comparison of two edge analyses ; (e) spectrum from the carbon-support before (white) and after (black) analysis of the pellet (the Cu peak is due to fluorescence of the support grid).

Damage to the heavy metal particles themselves may go so far as to destroy all trace of the particle after a few minutes /5/, limiting useful analysis times and attainable counting statistics. In the examples below the acquisition time was limited to 20 seconds.

The difference between "real" probe size and phase contrast image resolution has been pointed out by several authors /6,7/. Using a large beam defining aperture in the STEM it is possible to image for example the 0.45 nm planes of Al_2O_3 in conditions suitable for XES analysis (Fig. 2). In this case, however, the beam may in fact illuminate the specimen at large distances from the centre of impact.

Simple geometric optics calculations predict that the current density varies with distance from the optic axis as $r^{-4/3}$ at Gaussian focus, up to a value $r_m = C_s \alpha^3$, where C_s is the spherical aberration coefficient (3 nm in this case) and α the semi-angle of convergence of the beam. Increasing the beam convergence simply increases r_m , adding electrons at the edge of the probe. This will merely contribute to the background count and not increase the signal characteristic of very small particles.

5nm

Fig. 2 - Phase contrast image of the catalyst in electron-optical conditions used for XES analysis.

Following Oppolzer and Knauer /8/, the count rate in a characteristic peak for a spherical particle of radius a (whose thickness varies as $2\sqrt{a^2 - r^2}$) is :

$$R = \frac{I_B}{e} QW \frac{PN}{A} \frac{\Omega}{4\pi} \frac{\int_0^a 2\sqrt{a^2 - r^2} \cdot r^{-4/3} \cdot 2\pi r dr}{\int_0^{r_m} r^{-4/3} \cdot 2\pi r dr} \dots 1$$

where I_B is the total beam current, e the electronic charge, Q the ionization cross section, w the fluorescence yield, PN/A the atomic density and $\Omega/4\pi$ the solid angle of detection of the spectrometer. The limits on the upper integral will be zero to a or r_m whichever is the smaller, and for the lower integral zero to r_m . For beam widths very much smaller than the particle size (equivalent to the thin film case), equation 1 predicts a count rate proportional to size and beam current, whereas for $a < r_m$ $R = \text{const. } a^{5/3}$ where the constant is independent of r_m (and therefore of α and I_B).

Figure 3 shows experimental values of R for palladium particles (summing the Pd_L peaks with background subtracted) of radius 0.75 nm to 25 nm. Two aperture sizes were used $\alpha = 18.5$ mrad ($r_m = 19$ nm, $I_B \approx 4$ nA) and $\alpha = 8.5$ mrad ($r_m = 1.8$ nm, $I_B \approx 1$ nA). Also shown are the predicted variations using $Q = 2.2 \times 10^{-7}$ nm² /9/, $w = 0.05$ /10/ and $\rho N/A = 68$ nm⁻³. $\Omega/4\pi$ was calculated from thin film measurements to be 1.3×10^{-3} .

Although statistical uncertainties are rather large, due to the short acquisition times, agreement with the theoretical variation ($R = 4.5 a^{5/3}$ irrespective of which aperture is chosen) is good whilst in the case of the smaller aperture a trend towards linear dependence ($R = 10a$) is visible for particles greater than 5 nm in radius (i.e. for $a \gg r_m$). For the larger aperture linear dependence is expected only for particles greater than 50 nm in radius.

Fig. 3 - Count rate as a function of particle size for beam convergences of (a) 18.5 mrad and (b) 8.5 mrad.

The steeper dependence of count rate on size for small particles is due to electrons at the edge of the probe not interacting with the particle. Thus whilst for thin films the count rate (for Pd_L) would be 0.5 c/s per atomic layer even at monolayer thicknesses, extrapolation of the results presented here down to the case of a single atom predicts a count rate of 0.03 c/s. This is well below the background level typical of the support (~ 0.4 c/s) under the same illumination conditions, but extraction replicas on thin carbon films may present a great advantage.

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