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APPLICATIONS OF ELECTRON MICROSCOPY METHODS TO CATALYST PROBLEMS *

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The importance of electron microscopy techniques in tackling catalyst problems is considered. In particular the use of the imaging and spectroscopy facilities of the scanning transmission electron microscope is discussed and illustrated with some recent studies of catalytic materials. The advantages of using non-penetrating incident beams in electron-energy-loss spectroscopy, and glancing incidence microscopy, are especially highlighted.

The significant role in catalyst studies, won for electron microscopy in various operating modes, has been the subject of several reviews in recent years [1–4]. Thanks to the continued development of new instrumentation and imaging techniques however, fresh possibilities are constantly opening up some of which we identify here.

Traditional atomic resolution or structure imaging, widely regarded as the most spectacular achievement of transmission microscopy, depends on coherent superposition of the scattering contributions of atoms lying in columns parallel to the incident electron beam [5–7]. Crystalline catalyst materials such as intercalated clay minerals and zeolites [8,9] have consequently been profitable objects for investigation but there have also been important advances in imaging the bulk and surface structure of small particles. The profile imaging method in particular is now providing some very striking observations including the facetting of platinum particles induced by sulphur [10] as well as dynamic surface processes on catalyst materials [7,11,12]. Practical heterogeneous catalysts are generally more complex objects but can contain regions sufficiently well-ordered to provide structure images good enough for phase identification even when other microanalytical information is lacking [13,14].

Characterisation of catalyst microstructure using conventional TEM has revealed new insight into many bulk catalyst phenomena. The unusual chemisorption properties of systems which exhibit the so called "strong metal-support interaction" have been linked to metal support alloying [15,16]. Also catalyst

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deactivation has been associated with particle coarsening as revealed by studies in which catalyst ageing is accelerated [17]. A mechanism for the subsequent catalyst regeneration involves the redispersion of some of the metallic phase as sub-nanometre particles [18], although identification of such particles in the CTEM is hindered by phase contrast from the support [19]. The advent of in-situ controlled-atmosphere TEM facilities [20] should enable catalyst microstructure to be studied under conditions more closely resembling the true working environment [21].

The dedicated scanning transmission electron microscope (STEM) has so far been less effective than conventional TEM for high resolution imaging but offers a range of additional imaging signals, several of which are very useful particularly in studies of less well-ordered catalysts [15,22–25]. By collecting with an annular detector the electrons scattered through angles of about 5° for instance, one obtains an image which is less dominated by multi-atom superposition effects and is more directly dependent on the atomic number of individual atoms. This so-called Z-contrast technique has been particularly useful for revealing small heavy-atom clusters such as Pt on typical light atom supports such as charcoal, silica or alumina. A somewhat more demanding example of Ru on charcoal is

Fig. 1. Z contrast image of Ru particles on a high surface area carbon support.

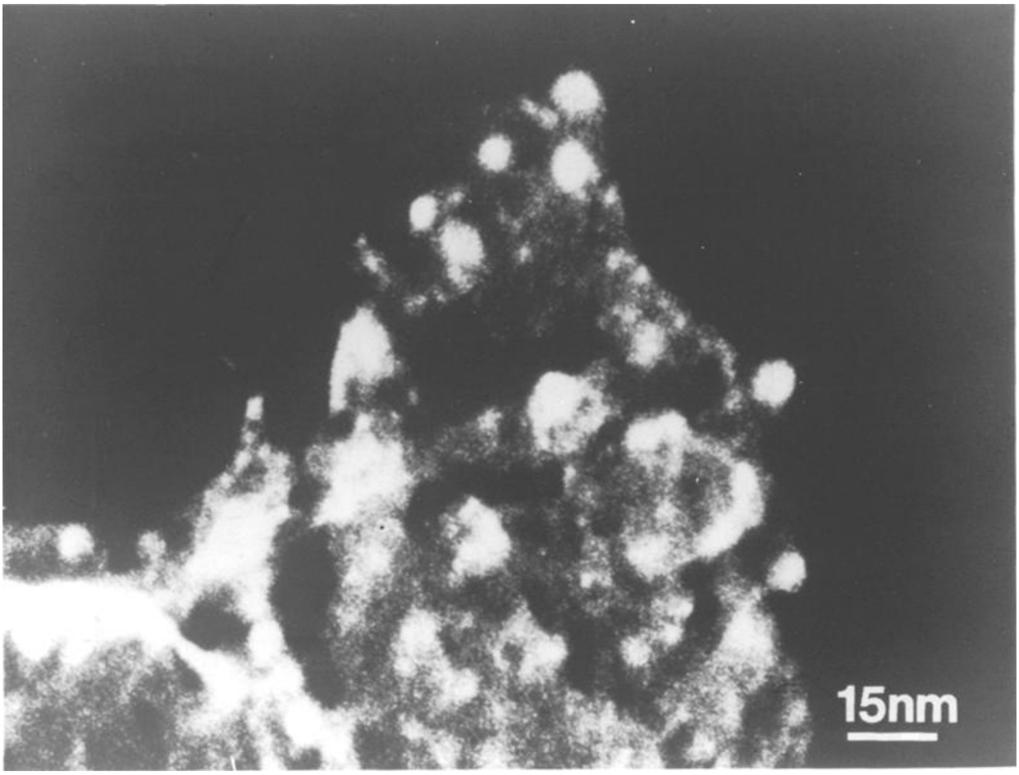

Fig. 2. High resolution secondary electron image of same area as fig. 1.

shown in fig. 1. For cases like Cu particles on thoria supports however, the Z contrast method is likely to be ineffective.

A very exciting recent development has been the introduction of high resolution pole-pieces for the STEM allowing Z contrast images to be obtained at atomic resolution [26]. It has been shown [27] that platinum clusters of three atoms can be detected on 20 nm thick Al_2O_3 supports and that cluster shapes and sizes can be quantitatively assessed from the integrated annular detector signal.

The secondary electron signal in the STEM provides very useful information about surface topography at a spatial resolution of about 1 nm [28]. Stereo-imaging of heterogeneous catalysts using a mixture of annular dark field and secondary electron imaging can provide a very detailed local picture of the three dimensional disposition of the small particles within the porous structure of the support material [29]. Figure 2 shows a high resolution secondary electron image of the region already imaged in fig. 1 by the annular dark field method.

Combined secondary electron imaging and spectroscopy detection systems are now available for the STEM [30]. These will undoubtedly provide useful, more surface-specific information since even if it may be difficult to image local differences in work function [3,31], the ability to carry out Auger spectroscopy at

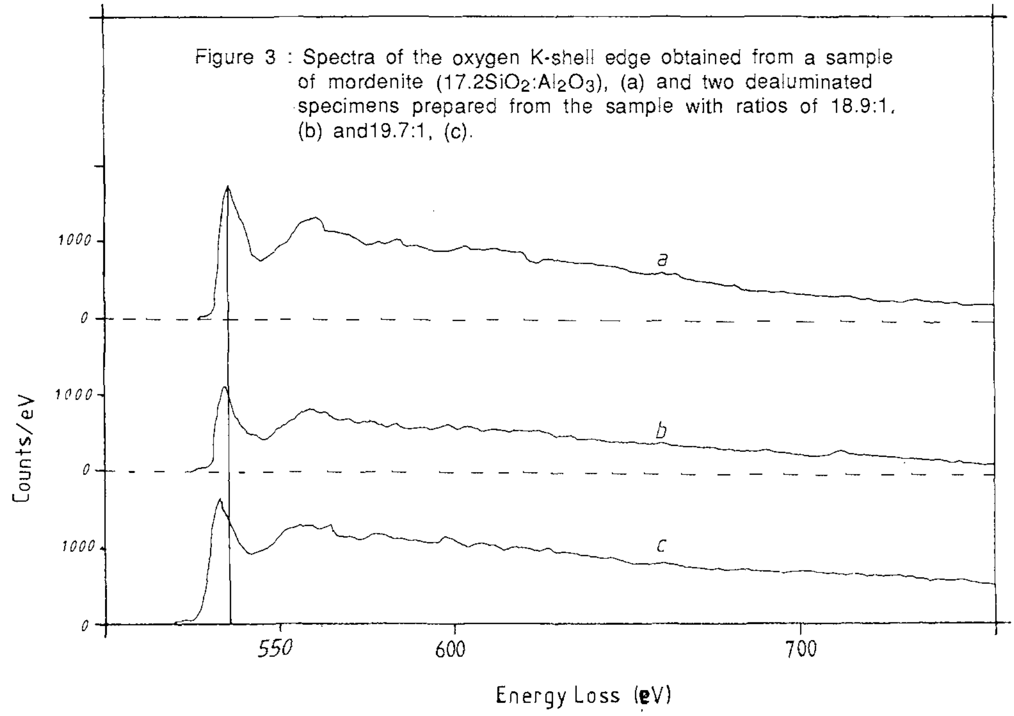

Figure 3 : Spectra of the oxygen K-shell edge obtained from a sample of mordenite ($17.2SiO_2{:}Al_2O_3$), (a) and two dealuminated specimens prepared from the sample with ratios of 18.9:1, (b) and19.7:1, (c).

Fig. 3.

spatial resolution approaching perhaps 2 nm should answer many questions about the distribution of catalyst promoters and poisons.

Other STEM imaging modes which are well established for catalyst characterisation include microdiffraction [32–35] and nanoanalysis based on X-ray emission [23,36–39] or the characteristic inner shell excitation features in energy loss spectra [40]. Detailed analysis of the shifts in position and changes in shape of these features should provide very signficant local chemical information about the catalyst itself as well as about carbonaceous deposits [41]. For example, studies of the oxygen K-shell edge of dealuminated zeolites carried out in Cambridge have revealed a dependence of the edge position on the concentration of aluminium in the sample as shown in fig. 3. This has yet to be correlated with similar shifts observed by other workers in less well localised XPS studies [42].

The problem of electron beam damage of specimens in the electron microscope is an everpresent one and has been addressed, particularly in the case of zeolites, by several authors [6,43]. Many techniques have been developed to minimise the electron beam-specimen interaction and so reduce the effect of damage [44]. In the case of energy loss spectroscopy the problem will be somewhat reduced by the introduction of parallel recording systems to replace the present serial acquisition devices. Energy loss spectroscopy has a major role to play in analysing beam-sensitive specimens. In particular the plasmon and other valence excitations studied in the low loss region of the energy loss spectrum are of much greater intensity than those signals detected at higher energy loss making the former a very attractive area of study if electron beam damage is significant. This region of the energy loss spectrum has been the subject of considerable recent activity and can be quantitatively analysed using classical dielectric theory. In addition to the more common transmission geometry the ability to collect signals in this region using a non-penetrating incident beam and describe the spectra using dielectric theory means that localised low loss spectroscopy is emerging as a crucial area of electron microscopy [45]. This is enhanced by the utilisation of effective medium theory to describe the low loss spectra of small particles embedded in a support matrix [46], and illustrates how this type of spectroscopy may be applied to catalyst studies. Detailed dielectric modelling of individual small particles, or complex catalyst media containing pores as well as small particles may thus provide a useful characterisation procedure bridging the gap between traditional macroscopic measurements on the one hand and high resolution microscopy on the other.

Another exciting development in bulk sample studies in the last few years has been the use of reflection electron microscopy (REM) at glancing angles to study

Fig. 4. REM image showing steps approximately 150 Å in height on the surface of a zeolite crystal. The magnification in the y-direction is reduced by about ×7 relative to that in the x-direction due to the glancing angle of the incident beam.

the surface [47]. This technique has successfully been used to image defects in non-catalytic materials [48] and has recently been applied to large zeolite particles. A typical REM image of the surface of one of these particles is shown in fig. 4 and surface steps of 100–200 Å in height can be easily observed.

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