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Published online: 25 Nov 2016.

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Some considerations related to the use of the Scherrer equation in powder X-ray diffraction as applied to heterogeneous catalysts

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Abstract This short overview summarises some of the basic considerations which should be undertaken when the Scherrer equation is applied to reflection widths in X-ray diffraction patterns of heterogeneous catalysts in order to extract meaningful information. Frequently, little account has been taken of the apparent complications arising from the presence of microstructural strain and disorder such as that which can be introduced upon doping or of anisotropic effects and such considerations are highlighted.

Graphical abstract Scanning electron micrograph showing the highly anisotropic nature of biogenic iron oxide found in a natural iron ochre source.

Keywords Scherrer equation, Crystallite size, Williamson–Hall, Microstrain
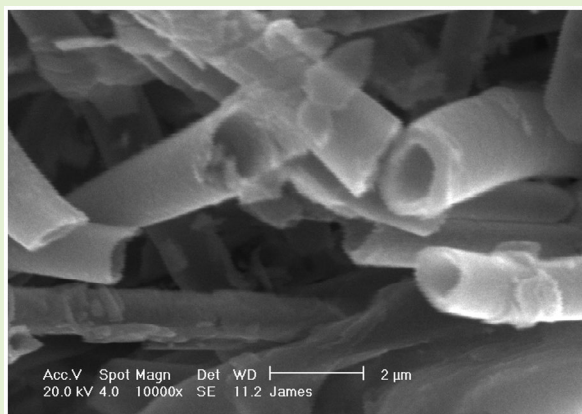
The application of powder X-ray diffraction for crystalline phase identification is ubiquitous in heterogeneous catalysis.[1,2] The use of the Scherrer equation, with the intended aim of the determination of crystallite size, is becoming more and more common in the literature. However, in reliably applying this analysis, it is necessary that due consideration is given to a number of important, and potentially complicating, considerations. In many analyses which have been undertaken, it is evident that such considerations have not been made with the consequence the resultant information may be, at best, meaningless. In this brief critique, which does not cover the effects of thermal broadening, such considerations will be outlined and related illustrative examples taken from the literature will be provided. The intention is to provide an appreciation of some of the considerations to be made in laboratory based analyses. More sophisticated refinement methods are not covered, although mention is made of some approaches which can be adopted to deconvolute size and microstrain effects and also to determine size distributions to provide an indication of the level of information which might be obtained.

The basis of the Scherrer equation (which has sometimes been incorrectly referred to by some authors as the Debye–Scherrer equation in apparent confusion with a powder X-ray diffraction

experimental method) is that the width of a powder X-ray diffraction reflection relates to coherent diffraction domain size.[3,4] It is important to remember that this dimension is perpendicular to the diffraction plane being analysed and also that it is strictly the *coherent diffraction domain size* which is being determined, rather than a crystallite size – a distinction necessary in systems comprised of multidomainic crystallites. The basis of the analysis is that the reflection width increases with decreasing coherent diffraction domain size (and in practice reflections are generally only observable relating to sizes above ca. 30 Å.) The relationship, which was first published by Scherrer in 1918,[3,4] can be given as:

$$d = \frac{K\lambda}{\beta \cos\theta}$$

where: d = coherent diffraction domain size, λ = the wavelength of the X-ray source applied, β = the reflection width (2θ), θ = the Bragg angle and K = the shape constant.

Of course, for the analysis to be meaningful, the reflection width must be purely that pertaining to the material itself and should consequently be free from effects such as those arising from instrumental broadening or the use of non-monochromatic X-ray sources (such as could arise from the α_1 and α_2 components of a laboratory Cu K$_\alpha$ source, for example.) Instrumental effects generally result in an upper limit of coherent diffraction domain sizes of ca 1000 Å in

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terms of the usefulness of the Scherrer equation. Using an appropriate standard, the degree of contribution of instrumental broadening (which can significantly influence line profile analysis) can be determined and taken account of. The value of the shape constant K which should be applied is dependent upon a number of factors including crystal morphology,[5] the specific reflection being analysed,[5] the form of the reflection width determined such as the integral breadth or the full width half maximum and even sample inhomogeneity through coherently diffracting size distributions.[6] In practice, the full width half maximum is the measure of reflection width most frequently used and the shape constant is commonly taken to be ca. 0.9 independently of morphology or reflection index. For dimensional consistency, it is important to appreciate that this value is expressed in radians, so that if a value of 0.9 is used, then the value for β, the reflection width, should also be expressed in terms of radians. It has to be said that upon inspection of the literature, very many instances can be found where the selection of the reflection for analysis appears somewhat arbitrary. However, this aspect needs to be carefully considered since it might have a profound influence upon the resultant analysis. For example, for a material comprising highly anisotropic crystallite morphology such as needle, disc or lathlike shaped crystallites, analysis of X-ray reflections sensitive to the axial dimensions for perfect crystals can be expected to differ markedly from those expressing radial dimensions. Indeed, such an approach provides the possibility of determination of morphology from X-ray powder diffraction patterns in selected circumstances. As an illustrative example, this has applied to the determination of the morphology of MgO powders prepared by different routes where a degree of correspondence has been found with accompanying TEM studies.[7,8] Due to considerations related to the possibility of overlapping reflections and broadening associated with increasing 2θ, appropriate caution is necessary when undertaking comparisons within different regions of a given powder diffraction pattern. Modern software will often take account of this by providing an average size determined from a number of peaks. However, the question again arises as to the usefulness of such an average, particularly in those instances where there is marked anisotropy.

Another aspect, seldom considered, is the contribution of strain and/or disorder to the reflection being analysed. Such contributions increase reflection width, with the net resultant effect being that if they are not accounted for in the analysis, the application of the Scherrer equation will lead to an *underestimate* of the coherently diffracting domain size. Therefore, in order to obtain rigorous data, deconvolution of the contributions of size and strain/disorder would be necessary. For selected systems, it is possible to account for this aspect by application of the Williamson–Hall method, which was based upon the additive effects of different angular dependencies of the size and strain functions for reflection widths.[9,10] Accordingly, the strain component can be expressed in terms of a strain index (η) possessing a $\tan\theta$ dependence, whereas as seen in the Scherrer equation, size has a $1/\cos\theta$ dependence. Since the reflection width could be comprised of the sum of the Scherrer and the strain components, it can be expressed as:

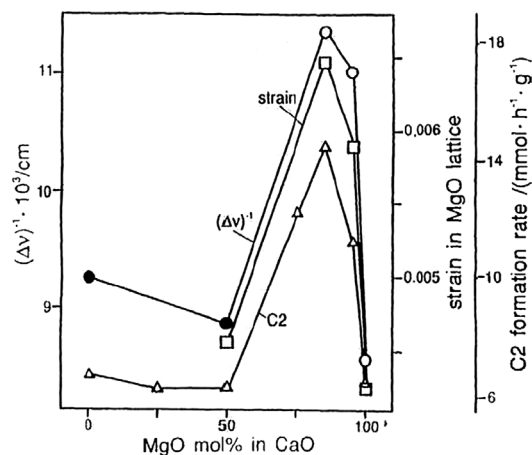$$\beta = \frac{K\lambda}{d\cos\theta} + \eta\tan\theta$$

Figure 1 Comparison of the reciprocal value of the wavenumber difference (Δu^{-1}) of the symmetric and symmetric CO stretching band (open symbols – room temperature, closed symbols – after heating to 600 °C), of the strain in the MgO lattice, and the C_2 formation rate as a function of composition for MgO/CaO catalysts for the oxidative coupling of methane, Figure reproduced from reference[11] with very kind permission from Elsevier

such that a plot of $\beta\cos\theta/\lambda$ as a function of $\sin\theta/\lambda$ would yield a straight line from which the size and strain information can be deconvoluted as the intercept and the gradient respectively. Related analyses have been undertaken to a limited extent in the heterogeneous catalysis literature and Fig. 1 provides an example of where the strain parameter has been argued to be of importance for the performance in MgO/CaO catalysed oxidative coupling of methane.[11]

As recognised in early work, however, there are again a number of limitations of the Williamson–Hall approach. Not least is the issue of complicating factors which may be introduced by overlapping reflections in powder X-ray diffraction patterns. Furthermore, as discussed above, there is no single numerical value of size for anisotropic morphology and also the strain contribution may have a strong directional dependence, again leading to marked anisotropic effects. An illustrative example of the influence of anisotropic disorder can be found in Fig. 2 which presents a set of powder X-ray diffractograms obtained for Zeolite β[12] in which stacking faults, known to be highly prevalent for this material,[12,13] can produce a significant differential broadening for the reflection occurring at 2θ of ca. 7.6°. Stacking faults are also known to be prevalent in a number of other catalytically relevant systems, such as cobalt metal[14] which again might produce significant limitations in the analysis of, for example, Co based Fischer–Tropsch catalysts. In other materials, the exact origin of pronounced reflection width anisotropy may be less well established such is in the markedly different widths manifested in the (1 0 4) and (1 1 0) reflections often observed in synthetic haematite prepared from goethite. In this case various explanations such as anisotropic morphology,[15] cationic disorder,[16] oxygen stacking faults,[17] twinning[18] and the development of porosity[19] have been advanced. Indeed sulfation of the precursor accentuates the differences in reflection width which has been attributed to a combination of the effect of morphology, cationic disorder and the development of axial porosity.[20]
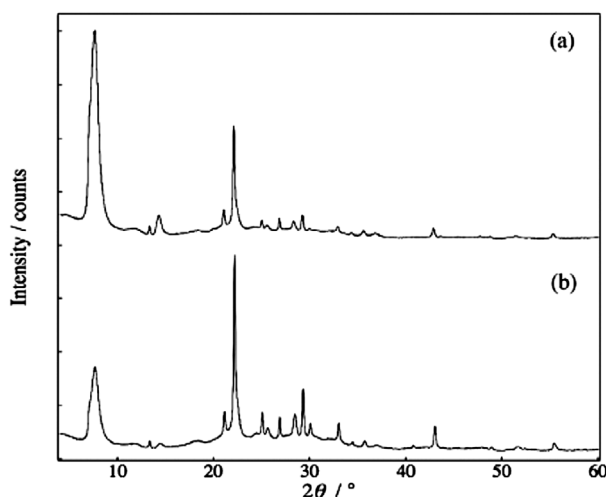
Figure 2   Powder X-ray diffraction patterns (Cu Kα radiation) of organic structure directing agent free Zeolite-β *a* after and *b* before dehydration. Figure taken from reference[12] with very kind permission from Elsevier

The example of Zeolite β in Fig. 2, as well as the cobalt and haematite systems, demonstrates both the limitations of simple non-comprehensively considered application of the Scherrer analysis to an arbitrary refection, for which no account has been taken to other contributing factors to its width. For highly directional effects, there would also been concerns in the application of the Williamson–Hall approach to all the reflections resulting from a single phase in a diffractogram. In the latter respect, therefore, the application of the Williamson–Hall method is most reliably based upon plots for families of related reflections, for which it is most reasonable to obtain single values for each of the size and the strain parameters. In view of the considerations of the potential anisotropic nature of size and strain effects, it is not surprising that strategies to account for this have emerged. In particular, Langford and co-workers have demonstrated the applicability of single reflection analysis across a diverse range of systems which have included cold worked nickel, nitrided steel, an electrodeposited nickel layer and a liquid quenched Al–Si alloy.[21] This based is based upon the Voigt function for which the Gaussian and Lorentzian contributions of single reflection profiles are deconvoluted and related to strain and size functions respectively. Whilst this level of detailed line profile analysis is very rarely encountered in studies of heterogeneous catalysis, it can prove very informative. An example of this type of situation is provided in a study of Ressler and co-workers in which the single reflection analyses have been undertaken for Cu and ZnO components of methanol synthesis catalysts.[22] Figure 3 presents the crystallite size and microstrain parameters as a function of catalyst composition determined from the Cu(1 1 1) and ZnO(1 0 0) reflections. In this study, it was reported that a direct correlation could be found between the turnover frequency of the materials for methanol synthesis and the microstrain parameter for the Cu(1 1 1) reflection as shown in Fig. 4. This is a particularly interesting observation since it demonstrates that Cu surface area alone cannot account for the observed catalytic behaviour. Subsequent work has related enhanced methanol steam reforming performance to the improved interaction of strained copper particles with
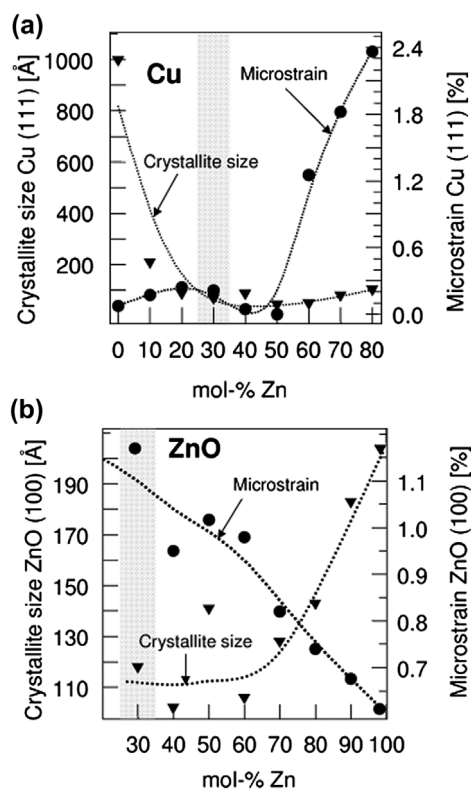

Figure 3   Microstrain and size parameters determined for Cu/ZnO catalysts for the Cu(1 1 1) and ZnO(1 0 0) reflections. Figure reproduced from reference[22] with very kind permission from Springer

the ZnO interface.[23] It is of interest to note that a very detailed and comprehensive discussion of microstructural and defect analysis with respect to diffraction and electron microscopy undertaken on the Cu/ZnO system has recently been publis hed.[24]

For catalytic applications, it is often informative to obtain information about the crystallite size distribution for materials. Its effect on powder X-ray diffraction line profiles has been outlined.[25] In appropriate circumstances, it is possible
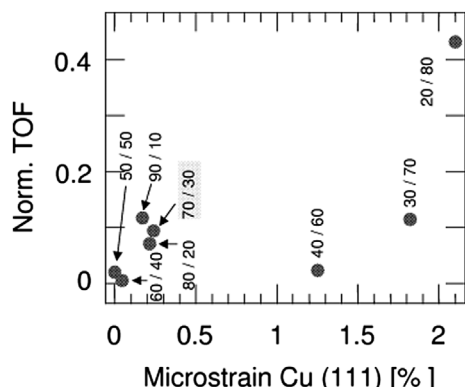
Figure 4   Normalised methanol synthesis turnover frequency as a function of Cu(1 1 1) microstrain. Figure reproduced from reference[22] with very kind permission from Springer

to obtain information on distributions when powder X-ray diffraction pattern analysis is undertaken using the Warren-Averbach approach.[26] This approach involves fitting profiles using a Fourier series, as detailed elsewhere.[3] Once account is taken of the effects of instrumental and microstrain broadening effects, average size can be extracted form the first derivative of the cosine coefficients with the size distribution being evident from the second derivative.[27] There are relatively few examples of the application of this method for the extraction of size distributions in the literature related to catalysis. However, this method has been shown to yield Pt crystallite size distributions comparable with those obtained by standard chemisorption methods for Pt/SiO_2 catalysts. In principle, the application of a powder X-ray diffraction based method can represent a significant advantage over TEM based methods when the statistical limitations of the latter approach are taken into consideration due to the improved sampling associated with the diffraction measurement. In terms of making direct comparisons between the results of various techniques, caution must be taken in terms of weighting, with the Warren-Averbach approach resulting in data directly comparable to that obtained from standard chemisorption techniques (as opposed to methods based upon analyses based on full width half maxima and integral breadth) but not TEM.

In summary, the above discussion is intended to highlight a number of limitations to the simple application of the Scherrer equation to heterogeneous catalysts which is increasingly a feature of published studies. Initial critical consideration should be given to the value and necessity of the information to be gained and, if such analysis is going to be informative, appropriate account should be taken of the various limitations mentioned which include the various contributions of instrumental broadening, morphological effects and disorder to reflection widths, as well the potential complication of their anisotropy. It should always be borne in mind that analyses relate to coherent diffraction domains rather than crystallites *per se*. In the appropriate situation with the correct approach, line profile analysis can potentially be very powerful and informative in determining the relationship of catalytic performance to the properties of bulk crystalline phases. In such instances, it is prudent to compare analyses from a variety of complementary techniques to evaluate consistency. In

inter-relating bulk crystalline structural properties and catalytic behaviour, is also important to bear in mind the role of surface structure, which is of course of paramount importance in heterogeneous catalysis, and surface sensitive analyses should be undertaken accordingly.

Conclusions

The above outline is intended to illustrate some of the basic, and sometimes neglected, considerations which should be undertaken in line profile analysis of powder X-ray diffraction patterns. Inspection of the heterogeneous catalysis literature shows that the application of the Scherrer equation for the determination of crystallite size is now near universal with, in most instances, little or no apparent acknowledgement being made of its limitations and the consequent usefulness and reliability of the parameter obtained. Accordingly, often the value of the information yielded is open to question whereas, in contrast, in some systems, the application of more sophisticated analyses can lead to identification of microstructure-function relationships as illustrated in the cases of the CaO/MgO and Cu/ZnO examples mentioned. The intention of this brief overview is to highlight some of the limitations to the analysis of X-ray diffraction widths presented in the literature. The interested reader is directed to more detailed treatments of the various approaches available.

Acknowledgements

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