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Modelling and Validation of Particle Size Distributions of Supported Nanoparticles using the Pair Distribution Function Technique

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ynopsisThe log-normal particle size distributions of supported nanoparticles were obtained from the Pair Distribution Function and the results were validated with Scanning Transmission Electron Microscopy.

bstractThe particle size of supported catalysts are a key characteristic for determining structure-property relationships. In this work we use the pair distribution function (PDF) technique to obtain the particle size distribution of supported Pt catalysts as they grow under reduction thermal conditions. The PDF of Pt nanoparticles grown on zeolite X was isolated and refined using two models: a monodisperse spherical model (single particle size) and a log normal size distribution. The results are compared and validated using Scanning Transmission Electron Microscopy results. In general, it is observed that both models describe the same trends in average particle size with temperature, but the results of the log-normal size distributions normalized by the volume to obtain the number-weighted distributions can accurately describe the mean size and the width of the size distributions obtained from STEM. This work confirms that, for small well-ordered supported nanoparticles, refinement of crystallite size distributions from the PDF yields accurate mean particle sizes and distributions.

eywords:Pair Distribution Function; Particle Size Distribution; Supported Catalyst; Scanning Transmission Electron Transmission Microscopy

1. Introduction

The analysis of particle size distributions (PSDs) is very important for reactions that are sensitive to the catalyst sizes, such as those involving the cleavage of molecules such as CO, O₂, N₂, NO, CH₄, NH₃, and C-C (Van Santen, 2009). PSDs are observed in supported (Treacy, 1999; Zhang et al., 2015; Mitrikas et al., 2001; Schaumberg et al., 2015) and unsupported metal catalysts (Schaumberg et al., 2015; Mahajan et al., 2015) and occur because during their growth catalysts follow multiple agglomeration steps with different rate constants (Finney et al., 2012), resulting in particles with different diameters. (Bayram *et al.*, 2015)

The PSDs of metal nanoparticles supported in zeolites can be more complex because the particle sizes are also affected by the zeolite pore and channel sizes (Gates, 1995), the composition of the framework (Samant & Boudart, 1991), and the synthesis method (Gallezot et al., 1975; de Graaf et al., 2001). Catalysts supported in zeolites are generally effectively confined within the pores, ranging in diameter between 1-2 nm, and are not detected by conventional X-ray diffraction (Choi et al., 2010).

In this work we show that using the total scattering Pair Distribution Function (PDF) technique it is possible to obtain accurate mean particle sizes and particle size distributions when studying the growth of Pt catalysts supported on zeolite X. The PDF describes the distribution of distances between pairs of atoms (Egami & Billinge, 2012; Billinge & Kanatzidis, 2004). A structural model can be refined with this technique and the program PDFfit2 and its graphic interface PDFgui (Farrow et al., 2007) allow the refinement of the structure of nanoparticles by attenuating the bulk calculated PDF $G(r)_{Bulk}$ by a function of finite particle size and shape, $\gamma_0(r)$. Assuming a monodisperse model (MM) the reduced pair distribution function, $G(r)$ of a uniform nanoparticle can be written as (Farrow & Billinge, 2009; Kodama *et al.*, 2006):

$$G(r)_{nanoparticle} = G(r)_{Bulk}\gamma_0(r) \quad \text{Equation 3.1}$$

$$\gamma_0(r)_{MM} = \left[1 - \frac{3r}{2D} + \frac{1}{2}\left(\frac{r}{D}\right)^3\right]H(D - r) \quad \text{Equation 3.2}$$

where D is the mean particle size and H is a Heaviside step function which ensures that the signal is zero at distances larger than the particle diameter (Guinier & Fournet, 1955).

The mean particle sizes obtained with PDF refinement results were proven consistent with Transmission Electron Microscopy (TEM) and UV-Vis Spectroscopy for unsupported nanoparticles (Masadeh et al., 2007). For supported nanoparticles a pair distribution function can be obtained by subtracting the scattering contribution of the support with sufficient accuracy that the resulting

difference-PDF may be used to refine the particle structure and size (Chupas *et al.*, 2007; Chupas *et al.*, 2009; Shi *et al.*, 2013; Terban *et al.*, 2015; Shatnawi *et al.*, 2007). The mean particle size obtained by this method using the monodisperse model has also been found consistent with TEM results (Shi *et al.*, 2013).

More recently, the program DiffPy Complex Modelling Infrastructure (diffpy-CMI) was developed which allows the refinement of a structural model using any shape function, including particle size distributions (PSD) (Juhás *et al.*, 2015). As described in the Supplementary Material, a log-normal size distribution (LNSD) is adequate to describe the major PSD observed in the Scanning Transmission Electron Microscopy (STEM) images for the catalysts reduced up to 300°C and 350°C. This distribution is used regularly to describe the PSD of other materials (Mitrikas *et al.*, 2001; Schaumberg *et al.*, 2015; Leoni & Scardi, 2004). For this distribution the form factor $\gamma(r)$ is defined as:

$$\gamma_0(r)_{LNSD} = 0.5 \operatorname{erfc} \left(\frac{-\mu - 3s^2 + \ln r}{\sqrt{2}s} \right) + 0.25r^3 \operatorname{erfc} \left(\frac{-\mu + \ln r}{\sqrt{2}s} \right) e^{(-3\mu - 4.5s^2)} - 0.75r \operatorname{erfc} \left(\frac{-\mu - 2s^2 + \ln r}{\sqrt{2}s} \right) e^{(-\mu - 2.5s^2)} \quad \text{Equation 3.3}$$

Where μ and s are the location parameter and the scale parameter of the LNSD, respectively, which are related to the mean particle diameter, P_{size} , and the standard deviation, P_{sig} , obtained from PDF by:

$$s^2 = \ln \left(\left(\frac{P_{sig}}{P_{size}} \right)^2 + 1 \right) \quad \text{Equation 3.4}$$

$$\mu = \ln(P_{size}) - \frac{s^2}{2} \quad \text{Equation 3.5}$$

The LNSD refined from the PDF is then generated using:

$$F(r) = \frac{1}{rs\sqrt{2\pi}} \exp \frac{-(\ln r - \mu)^2}{2s^2} \quad \text{Equation 3.6}$$

In this work we show that, although both the MM and LNSD yield similar particle size trends in our samples, the results obtained by the normalization of the LNSD describe more accurately the experimental particle size distribution observed in STEM. The particle sizes obtained by X-ray scattering describe the volume-weighted size of the crystallite domain. Microscopy techniques, on the other hand, are used to obtain number-weighted particle sizes that may contain multiple crystallites. Thus, the agreement between the PDF and STEM results suggests that a large number of particles are monocrystalline and well-ordered. Moreover, this work shows that this technique is suitable to study the structure and size distribution of supported nanoparticles.

2. Methodology

Details on the sample preparation and characterization with Scanning Transmission Electron Microscopy are found in the Supplementary Information.

2.1. Synchrotron Data Collection

The X-ray scattering experiments were carried out at the 11-ID-B beamline of the Advanced Photon source at Argonne National Laboratory. Diffraction data were collected using a two dimensional amorphous silicon flat panel detector from Perkin-Elmer. A sample to detector distance of 20 cm and a maximum 2-theta scan angle of 50° were used. The powder samples were analyzed in transmission geometry, with an X-ray wavelength of $\lambda=0.2128$ Å. The two-dimensional data were integrated and converted to one-dimensional intensity versus 2-theta using the FIT2D program (Hammersley et al., 1996).

Scattering data was obtained for the calcined Pt/NaX sample packed inside a polyimide capillary (Cole-Parmer, 1.1 mm OD and 1 mm ID, part number 95820-09 manufactured by MicroLumen, Inc) while it was reduced *in situ* in 5% H₂/Ar with a heating rate of 5 K/min from 323 K to 623 K and a hold time of 10 min at 623 K.

2.2. PDF refinement

To obtain the PDF of the Pt nanoparticles, the scattering of the NaX support was subtracted from the scattering of the reduced Pt/NaX sample at the same temperature using the PDFgetX3 program (Juhás et al., 2013). The scale of the scattering data of the support was chosen to optimize the quality of the resulting PDF.

Refinements with the monodisperse spherical nanoparticle model (MM) and those using the log-normal spherical distribution model (LNSD) were done with Diffpy-CMI (Juhás et al., 2015). In both models the same parameters were refined up to an interatomic distance of 40 Å starting with a scale factor, isotropic thermal factor, an r -dependent sharpening term, and the crystallite size parameters. Refinement with the monodisperse particle model yields only a mean size (D), while refinement with a log-normal distribution model yields a mean particle size (P_{size}) and the standard deviation of the distribution (P_{sig}).

3. Results

Refinements of the differential Pt PDFs using the MM resulted in goodness of fit values R_w that ranged from 18.5%-31.8% for all the reduction temperatures (Figure 1). The residuals improved with increasing temperature as the scattering signal from the growing Pt nanoparticles increased. The higher values of R_w at low temperatures are due to errors in the subtraction of the support scattering, possibly caused by local distortions of the support structure by the presence of the nanoparticles, and

manifested primarily as a strong positive peak at 1.69 Å coupled with a negative peak at 2.38 Å, and small ripples continuing out at higher- r . Some residual signal from the support will result in larger R_w values for nanoparticle model fits, but are unlikely to introduce significant bias since there are no peaks in the nanoparticle models at exactly those locations, and indeed, this is our observation here. This effect is reduced at 623 K due to larger nanoparticles migrating to the surface of the support, as suggested by STEM images (see Supplementary Material), and the overall greater relative scattering signal from larger nanoparticles.

Figure 1 Refinement fits of the Pt PDFs at 518 K, 573 K, and 623 K.

The refinements using the LNSD resulted in similar R_w values to the MM models, thus both particle size models are able to fit the differential PDF with similar accuracy. The mean sizes obtained with both models follow a similar trend at all the reduction temperatures which suggest a jump in growth between 573 K and 623 K (Figure 2). However, the refined values of the mean crystallite diameter in the MM models are 8.2-12.9% larger than the mean of the LNSD. This is not surprising because the log-normal distribution is asymmetric. This result shows that, for these particles, the PDF cannot be used by itself to differentiate between the presence of monodisperse spherical nanoparticles and a log-normal size distribution of spherical nanoparticles.

Figure 2 Refined mean particle sizes during the *in situ* reduction using a spherical MM (D) and LNSD model (P_{size}).

The limitation in sensitivity of the PDF method for studying particle size and shape is known [(Farrow *et al.*, 2014)] and is widely exploited in nanoparticle modelling where fine details of the nanoparticle crystallite morphology are not the target of the research. In this work the goal was to determine whether reliable quantitative information about log-normal distribution parameters may be refined from the PDF, even when the LNSD model does not give a lower R_w than the MM model. For this, the particle size distributions were obtained by measuring particle diameters from STEM images. STEM has the advantage of giving very direct information about nanoparticle sizes, but the disadvantage of being slow and tedious and not necessarily resulting in a representative sample average since only a small part of the specimen is sampled. It is also very difficult to obtain information on structural changes occurring *in situ* with this technique. Getting this information directly from the PDF is, thus, very valuable. These two techniques, however, measure different quantities: STEM yields the particle size and PDF the size of the domain of coherent structural order, or “crystallite” size. The two are the same only in structurally well-ordered nanoparticles and in general the particle size is an upper bound on the crystallite size. Here we find excellent agreement between the STEM and the PDF implying that the particles are single domain.

As explained in the Supplementary Material, the STEM PSD of the sample reduced up to 623 K can be described as monomodal, while the STEM PSD histogram at 573 K is more accurately described as bimodal but the contribution of the second mode at higher particle sizes is small so only the main distribution was considered (Figure 3). In order to reliably compare the histograms obtained by STEM and PDF, the LNSD obtained with the latter was normalized by the sphere volume (r^3) and then rescaled to obtain the number-weighted distribution. This normalization displaces the curve to lower size-values. The resulting number-weighted distribution derived from PDF agrees rather well with the STEM histograms.

Figure 3 Histogram of the STEM results (bars) with the results of the log normal size distribution (LNSD) and the mean diameter (D) obtained for the MM obtained from the sample reduced to (a) 573 K and (b) 623 K.

Table 1 compares the mean particle sizes obtained by refinement of the PDF and the values obtained by fitting a LNSD to the primary distribution of the STEM results at 573 K and 623 K. While the number-weighted LNSD obtained from PDF overestimates the mean size, the error is within ± 0.3 nm.

Considering that the goodness of fit parameter R_w was 30.2% at 573 K, the accuracy of the LNSD is encouraging. The mean values obtained from PDF refinement could be skewed higher by the presence of larger particles not fit by the monomodal distribution. This is an important result as it suggests that this technique is reliable to study the changes in average particle sizes of supported nanoparticles *in situ* even when they are still very small. In comparing the crystallite size distributions obtained from PDF and particle size distribution from STEM, the agreement suggests that the supported particles are monocrystalline and ordered in an fcc configuration at 573 K and 623 K.

Table 1. Comparison of the mean particle sizes obtained from refinement of the PDF with the MM (D), the volume-weighted LNSD (P_{size}), the number-weighted LNSD (D_{NW_LNSD}) and the values obtained by STEM (D_{STEM}) for the samples reduced at 573 K and 623 K.

Temperature (K)	Particle size and percentage of range(nm)	$D_{STEM}(nm)$	$D_{NW_LNSD} (nm)$	$P_{size} (nm)$	D(nm)
573	0.7-2.5 (81%); 3.0-56.8(19%)	1.2	1.4	1.6	1.9
623	0.8-5.6(95%): 7.6-47.7(5%)	2.6	2.9	3.3	3.6

Assuming the same accuracy applies from 518 K to 623 K where Pt fcc peaks are observed, Figure 4 shows the trend in the number-weighted LNSD obtained from PDF. It shows, similar to Figure 2, that the mean particle size increases with temperature with a distinct jump between 573 K and 623 K; it also shows that the particle size distribution broadens with temperature. This information is consistent with agglomerative sintering of the particles (Bayram *et al.*, 2015) where particles of different sizes coalesce with each other yielding a wider distribution of particle sizes. The source of this sintering was discussed previously (Gómez-Mendoza *et al.*, 2015) but, in general, these results suggest that if the reduction step would stop at 573 K the synthesis would produce small monodisperse ordered catalysts that are mainly contained within the pores of the support.

Figure 4 Number-weighted log-normal distributions obtained through refinement of PDFs from sample reduced from 518 K to 623 K.

4. Conclusions

This work describes a method to obtain particle size distributions of supported catalysts by refinement of their pair distribution functions that can be compared directly to experimental distributions obtained by microscopy techniques. It shows that a number-weighted log-normal particle size distribution (LNSD) obtained from PDF is in good agreement with that obtained from STEM imaging for these Pt nanoparticles. Since PDF actually measures crystallite size, which may be smaller than particle sizes, these results show that these particles were well-ordered single-domain entities.

The three models studied (MM, volume weighted LNSD, and number weighted LNSD) described the same trends in particle growth with temperature in a semi-quantitative fashion. In the studied case this was true even when the goodness of fit parameters are higher due to the presence of spurious peaks from imperfect subtraction of the support suggesting that this technique is very sensitive to the particle size. The trend showed a jump in particle size between $573\text{ K} < T < 623\text{ K}$ that is consistent with agglomerative sintering. Sintering is ubiquitous in catalysts and information of the particle size distribution allows a better correlation between catalyst activity and their size.

More importantly, this work suggests that PDF is a reliable alternative to simultaneously observe how the PSDs and structure change with synthesis conditions which is a unique approach to design more active catalysts. Finally, this work shows the versatility of the DiffPy Complex Modelling Infrastructure (Diffpy-CMI) program to model deviations from an average model using PDF results to improve the accuracy of the results.

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