

# Use of Nanoparticle Tracking Analysis for Particle Size Determination of Dispersed Catalyst in Bitumen and Heavy Oil Fractions

Victor M. Rodriguez-DeVecchis,\* Lante Carbognani Ortega, Carlos E. Scott, and Pedro Pereira-Almao

Schulich School of Engineering, University of Calgary, Calgary, Alberta T2N 1N4, Canada

## Supporting Information

**ABSTRACT:** The use of nanoparticle tracking analysis (NTA) for size determination of nanocatalysts dispersed in bitumen or heavy oil fractions was investigated. A method for sample preparation is proposed, and comments on adaptation of the technique and troubleshooting are addressed and discussed. The NTA was able to measure the particle size of a trimetallic catalyst dispersed in bitumen obtaining a mode size of 111 nm, with particles ranging from 40 to 1000 nm and 80% of them between 57 and 176 nm. NTA data was compared to the particle size obtained by depositing the same catalyst on sand and analyzing it through SEM-EDX, obtaining the same particle size range. Refinement of the sample preparation method and measuring parameters are suggested.

## 1. INTRODUCTION

The measurement of particle size is of great importance in different applications over a wide range of industrial processes. Particle size substantially affects product quality, from food products to cement, emulsions, and aerosols.

The desired particle size varies for each application, some preferring large particles and some preferring particles as small as possible, that is, suspensions and emulsions. Other applications require particles in a specific size range to obtain the desired effect, such as pharmaceutical processes.

With the increase of the world energy demand, the exploitation of heavier oils and bitumen has significantly increased during recent years. As a result, the challenges to efficiently process these feedstocks have also increased. One of the most promising ways to tackle the challenges posed by heavy oils and bitumen is catalysis. However, conventional supported catalysts are not suited to process these kind of feedstocks because the porous supports are easily plugged by the large molecules present in bitumen and heavy oils, with the consequent loss of catalytic activity.

The development of dispersed catalysts, also used in pharmaceuticals, has provided an innovative pathway for the processing of heavy oil feedstocks. In these types of catalysts, the active phase is encountered on the surface of small particles that are nonporous and therefore do not have the risk of being plugged by large molecules present in the feedstock. The advantages of the dispersed catalyst involve high specific surface area and the ability to penetrate the network of heavy molecules in bitumen, among other advantages.

The preparation (method and conditions) of the dispersed catalyst has a direct effect on the resulting particle size and therefore has to be carefully controlled. A key step to do so involves an accurate measure of the resulting particle size, of which the effect of the different variables in the preparation cannot be accounted for.

There are several techniques available to measure small particle sizes, each of them with their own strengths and disadvantages. They can generally be classified into two groups:

single particle and ensemble measurement. The single particle techniques measure individual particle size and are usually based on high powered microscopes such as transmission electron microscopy (TEM), atomic force microscopy (AFM), and scanning electron microscopy (SEM).<sup>1–3</sup> The ensemble techniques are normally indirect techniques where all of the particles in the sample are measured at once. The most common of these are dynamic light scattering (DLS), laser diffraction (LD), and electrophoretic light scattering (ELS).<sup>2,3</sup>

The selection of the measuring technique has to be carefully considered on the basis of several parameters such as the range of the particle size, the amount of sample available, and other specific conditions concerning the nature of the particles and the media in which they are suspended, to guarantee a reliable, precise, and valid measurement.<sup>4</sup>

When dealing with bitumen or heavy oil fractions, a combination of different challenges arises for the measurement of particle size due to the nature and composition of the bitumens that serve as the continuous media. The high viscosity and black color pose the most significant challenges in terms of physical properties that can affect the measurement of particles dispersed in the medium. The presence of metals in the initial feedstock as well as clay particles still embedded in the oil matrix product of the exploitation can also be an important source of error. The presence of agglomerates of large molecules such as asphaltenes that can be mistaken by particles in some analyses is another factor to keep in mind.

We have developed a preparation technique to obtain dispersed catalyst on bitumen<sup>5</sup> that has been successfully tested under different processing conditions to upgrade bitumen and its heavy fractions. However, the determination of the particle size obtained in this preparation still has not been done.

**Received:** July 6, 2015

**Revised:** September 16, 2015

**Accepted:** September 18, 2015

**Published:** September 18, 2015



Several authors have attempted the measurement of these particles through various techniques, most of which required intermediate processing steps or the use of other hydrocarbon media. Alkhaldi (2013) used centrifugation after dilution to separate the particles and later let them dry at room temperature before using a TEM for particle size determination.<sup>6</sup> An alternative method is the deposition of particles on a sand medium with subsequent analysis in TEM and SEM. When observing their results, it can be noted that most of the particles are found in agglomerates of various sizes and the particle size is estimated by measuring what seem to be the constituent particles of the agglomerate. However, it is impossible to tell if the agglomerates were formed during the catalyst preparation (and therefore existed as though in the bitumen media) or if they are the result of the after processing steps.<sup>7–9</sup> Another source of incertitude in single particle techniques measurements is sample size. The total number of particles obtained in a preparation is unknown; therefore, it is difficult to select a sample size that will be representative of the whole, while analyzing the full sample is not an option.

A different approach for nanocatalyst size characterization was taken by Galarraga (2011), Thompson (2008), and Contreras (2010) where the catalyst was prepared directly in different hydrocarbon media such as base oil. Base oil is a clear hydrocarbon that allows the use of ensemble measuring techniques such as DLS.<sup>7,10,11</sup> The results presented by these authors show that particles can be measured using this procedure with acceptable levels of the polydispersivity index (PI), around 0.18 (a good PI is considered to be under 0.1, to ensure a monomodal distribution).<sup>7,10</sup>

Contreras (2010) and Hashemi (2012) tried the same approach by using vacuum gas oil (VGO) as the continuous medium; however, they faced problems regarding agglomeration and sample stability.<sup>11,12</sup> Another option has been to dilute the bitumen until the sample is sufficiently transparent. These approaches result in measures with high PI index in DLS, with several error warnings regarding the quality of the measurement due to the light pass and the possibility of settling of the particles, which creates high levels of uncertainty in the results.

The preparations in different hydrocarbon media (base oil and VGO) are valid only under the assumption that the preparation will not be affected by the difference in the nature of the continuous medium. Meanwhile, the dilution process may cause larger particles to drop out of the suspension, shifting the average particle size to a lower value and producing misleading results.

It has been reported,<sup>2,13,14</sup> after that for samples including particles that are not monodispersed, the results obtained via DLS are not reproducible even when samples are prepared by mixing two specific particle sizes. The particle size of the catalyst depends on the droplet size formed in the micro-emulsion, which is controlled by the degree of mixing achieved. This may be controllable at a lab scale, but even at a bench-scale pilot plant it is almost impossible to guarantee a monodispersed catalyst particle size; therefore, despite efforts in this regard, DLS seems an unfavorable candidate for characterization under these circumstances.

The nanoparticle tracking analysis (NTA) technique potentially combines the advantages of the single and the ensemble particle sizing approaches.<sup>2,14–16</sup> The NTA starts by identifying the particles suspended in the fluid within the viewing range. This is accomplished by the detection of

scattered light from the irradiation of particles with a laser, viewed through a charged couple device camera. Later, each particle's movement is tracked while inside the viewing range, calculating the particle size obtained by the relationship between the distance moved over a set period of time. The hydrodynamic radius of the particle is given by the Stokes–Einstein eq 1.<sup>2,15</sup>

$$\overline{(x, y)^2} = \frac{2kTt}{3r\eta} \quad (1)$$

where  $x$  and  $y$  are the position coordinates,  $T$  is the temperature,  $t$  is the total time a singular particle is tracked (s),  $k$  is the Boltzmann constant,  $\eta$  is the viscosity of the medium, and  $r$  is the hydrodynamic radius (m). Therefore, NTA follows and measures each particle individually as is done in single particle techniques, but repeats this procedure for all particles in view, as per ensemble techniques. It must be noted that the measured particles only count if they are tracked for a minimum amount of time. Anything tracked under this minimum time will not be counted in the final result.<sup>4</sup>

The NTA technique can detect particles as small as 9–15 nm in any solvent, so long as the particles scatter sufficient light to produce a signal.<sup>15</sup> The instrument requires temperature and viscosity data for the sample to calculate particle size. No additional pretreatment is required, except dilution to obtain an appropriate particle concentration for the NTA.<sup>15</sup>

NTA technology has been used to great success in biological and toxicological industry with many applications such as cellular vesicles,<sup>17</sup> drug nanoparticles delivery and protein aggregates,<sup>16</sup> and casein micelles<sup>18</sup> with very satisfying results.

The NTA technique results have been compared to both single and ensemble techniques. Boyd (2011) compared the results for TEM, AFM, DLS, and NTA using 100 and 200 nm supplied latex particles in water, finding comparable results and providing a good explanation of how the comparison should be performed.<sup>2</sup> Montes-Burgos (2011) also compared the performance of DLS and NTA techniques using gold nanoparticles in relevant biological media (plasma) for nanotoxicological purposes, again with satisfying results.<sup>14</sup>

On the basis of the inherent challenges of measuring the particle size of a dispersed catalyst in bitumen or heavy oil fractions and the different approaches and techniques employed until now to try to characterize such a catalyst, this work investigates the possibility of using NTA technology to measure the particle diameter of a dispersed catalyst in bitumen or heavy oil fractions. The necessary procedure to implement this technique in a fast and reliable manner to measure the particle size was developed.

## 2. MATERIALS AND METHODS

**2.1. Catalytic Feed Preparation.** The catalyst that was used in this work was a trimetallic nanocatalyst containing Ni, Mo, and W, prepared by the transient emulsion method<sup>19</sup> of athabasca bitumen (ATH) with aqueous solutions of the transition-metal salts: nickel acetate (98%, Aldrich), ammonium metatungstate (98%, Aldrich), and ammonium heptamolybdate (99%, Stream Chemicals).<sup>5</sup> A detailed description of the production of catalytic emulsions has been presented by Galarraga et al.<sup>20</sup> The preparation of the catalytic feed can be done in two ways: the first, in the laboratory, is where the aqueous solutions are added slowly to the bitumen while heating and stirring to ensure the proper dispersion.<sup>5</sup> The

second option employs a continuous mode of online compact preparation (manufacturing) unit (CMU) consisting of water solution pumps, bitumen pumps, and additives pump to drive the synthesis and a mixing zone with both static mixers and mechanical rotational mixers, followed by a decomposition zone from which the dispersed metal sulfides are obtained.

The final products are bitumen with incorporated nanocatalyst and a mixture of diluent and water. A general scheme of the CMU is shown in Figure 1.

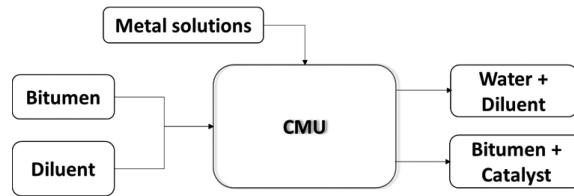


Figure 1. Catalyst preparation flow scheme.

In this work, the catalyst had a final target concentration of 1200 ppmw of metals with respect to the bitumen, distributed as follows: 211 ppm of Ni, 604 ppm of Mo, and 385 ppm of W.

**2.2. Sand Pack Catalyst Deposition.** The catalyst deposition over a sand pack was performed in a reactivity test unit (RTU3) using a vertical reactor in up flow configuration (35 cm long and 1 in. OD). The sand pack was prepared following the guidelines of Coy (2012) and Zamani (2010), using sand 70–100 U.S. sieve and synthetic brine at 1 wt %; the resulting packed sand media had a porosity around 35% and a permeability of 13.5 darcys, similar to and in accordance with the preparations presented by Coy (2012). The catalyst deposition consists of flowing the catalytic feedstock through the sand pack at a moderate temperature such that the viscosity is reduced enough for the catalyst particles to move and attach to the sand, producing no or very little conversion on the bitumen. On the basis of the works of Coy (2012) and Zamani (2010), the selected conditions were a temperature of 300 °C and 24 h of residence time based on the pore volume. Deposition was carried out over 9 days, monitoring the exit product in quality and metal content. Afterward, aliquots of the sand at different lengths along the reactor were taken and calcined in an oven under an air atmosphere at 500 °C for 12 h to later be analyzed by SEM-EDX.

**2.3. Simulated Distillation.** The liquid products at each stage of the process were analyzed through simulated distillation to observe their composition and detect any level of change in the feedstock. The results are reported in terms of typical cuts for the oil industry according to their boiling points: naphtha (IBP-216 °C), distillates (217–343 °C), vacuum gas oil (VGO) (344–550 °C), and vacuum residue or just residue (VR) (550+ °C). Errors obtained in SimDist are 1% relative for lighter fractions (naphtha, distillates, and VGO) and 4% relative for VR.

**2.4. Inductively Coupled Plasma-Atomic Spectroscopy.** An inductively coupled plasma (ICP) together with atomic spectroscopy (AS) (IRIS Intrepid II optical emission spectrometer-ICP spectrometer, Thermo Electron Corp.) was used to determine the amount of metals present in the bitumen before and after the incorporation of the catalyst as well as the amount of metals remaining in the sand pack after processing. The error of the technique is 1% in the concentration of each of

the metals. To transform the sample into an aqueous solution, phosphoric acid and nitric acid were added to an aliquot of bitumen and placed in a microwave digester (CEM Mars 6) before dilution to an appropriate concentration.

**2.5. Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy.** The sand samples collected at different heights along the reactor, after being calcined to remove the hydrocarbon phase covering them, were taken to a scanning electron microscope (FEI QUANTA FED 250) to analyze the surface of the sand and observe the deposited catalyst particles. The SEM is coupled with an energy dispersive X-ray spectrometer (EDX or EDS, BRUKER X FLASH 5030) that performs an elemental analysis over different zones (particles and background). This guarantees that the measured particles are actually catalyst particles and no other type of particles generated during handling and processing.

**2.6. Nanoparticle Tracking Analysis.** A sample produced during the catalytic feed preparation was set aside and taken for nanoparticle tracking analysis (NTA) using NanoSight NS300 equipment and NTA 3.0 software for the data analysis to obtain the diameter of particles suspended in the feed.

**2.7. Athabasca Bitumen Sample Preparation and Measurement with NTA.** On the basis of the previous discussion, the general sample preparation method proposed for NTA analysis of bitumen with dispersed catalyst is as follows: A sample of the ATH bitumen is diluted in toluene and submitted to mechanical agitation for 10 min. After we verified that there are no distinct phases, the mixture is sonicated for 10 min (Branson 3510, 100 W-42 kHz) to further increase the homogeneity of the sample. An aliquot is taken using a plastic syringe and injected into the NanoSight sample chamber. Making sure there are no visible bubbles in the chamber, the sample is flowed through the chamber (approximately 1 mL, 4 times the chamber volume, 0.25 mL). It is verified that there are no particles stuck in the chamber and a drift is induced. The focus and camera parameters should be adjusted to obtain the best possible view of the particles, following the guidelines provided by the equipment manufacturer,<sup>4</sup> although they have no influence on the final calculation. Five videos of 1 min length each are taken, advancing the sample between each video or leaving enough time for the drift to “replace” the sample. This allows the measurement of a larger variety of particles across the aliquot. The analysis settings are later fixed depending on what is observed in the videos.

Further dilutions are prepared by taking an aliquot of the already prepared sample and adding toluene. The mechanical agitation and ultrasound steps are repeated for each sample, and the procedure is repeated each time. Between samples, clean solvent (toluene) is flowed through the chamber (about 2 or 3 mL) to ensure no sample remains. This is confirmed with the camera to make sure the chamber is clean. If not, the chamber should be opened and cleaned manually.

### 3. RESULTS AND DISCUSSION

**3.1. Catalytic Feed Preparation and Sand Pack Catalyst Deposition.** The product quality was tracked at each step of the catalytic preparation and deposition process using SimDist. The cut distribution for each intermediate product is shown in Table S1. The simulated distillation allows one to detect changes in composition of the liquid in which the particles are suspended. Simulated distillation data are presented to show the effect of the processing stages on that suspending media, that is, during the stage of catalyst

manufacturing and the ulterior catalytic particles deposition under conditions that could be reactive for that suspending fluid.

The addition of gasoline (18 wt %) for the CMU processing is clearly observed in the increased naphtha fraction (feed CMU) as well as its almost complete removal when comparing the catalytic feed and the original bitumen.

The separation of the diluent is done at the same time as the water separation. The separation is performed in a hot separator after the decomposition zone in the CMU unit. In the separator, an inert gas (i.e., N<sub>2</sub>) is injected at the bottom to aid in the stripping to enhance the separation of the water and diluent.

During the catalyst deposition on the sand pack, intermediate samples were taken during the process. The results show a slight increase in the lighter fractions and the quality was consistent along the experiment, which serves as an indicator of correct operation of the unit.

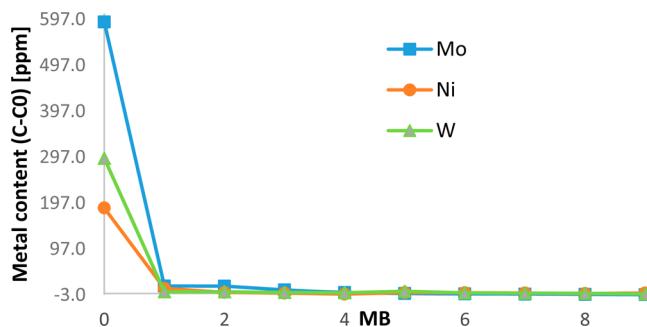
The metal content was measured using ICP-AS at each step of the bitumen processing. The original athabasca bitumen was analyzed in the absence of any manipulation to determine initial metal contents. These values were subtracted from the measurements of subsequent processing stages because the intrinsic metals are not incorporated into the active phase of the catalyst. The results of the catalytic feed preparation are presented in Table 1.

**Table 1. Catalytic Feed Preparation Metal Results**

	Mo (ppm)	Ni (ppm)	W (ppm)	total (ppm)
ATH (C0)	10.0	88.0	1.0	99.0
ATH + CAT	601.4	274.5	295.5	1171.4
incorporated by CMU	591.4	186.5	294.5	1072.4
desired	604	211	385	1200.0
difference	12.6	24.5	90.5	127.6
% error	2.1	11.6	23.5	10.6

Athabasca bitumen naturally has approximately 100 ppm of targeted metals, most of it nickel; this amount is subtracted for the catalyst incorporation and removal analysis. Negative values obtained for the metal content of a sample as compared to the feed meant that intrinsic metals were removed from the original bitumen during processing. The incorporated (dispersed) catalyst during the preparation was very close to the target value with a 10% margin of error. Tungsten measurements were determined to have the highest relative error, which was unsurprising considering ICP analysis is known to have a higher error rate for tungsten due to difficulties with the solubility of this element. During the sand pack decoration (catalyst deposition), the liquid product is sampled and analyzed every 24 h for metal content, to guarantee that the catalyst is being left in the sand and to calculate the amount of metals left in the sand. From the very beginning of the deposition process, almost all of the catalyst remains in the sand pack. This was found by metal analysis of the liquid product, which contained metals at levels similar to those of the initial bitumen or lower. These results are shown in Table S2 and Figure 2.

**3.2. SEM Results.** When the sand pack was removed, samples of the sand were taken approximately every 5 cm along the reactor starting from the bottom, because the reactor was operated in an up-flow configuration. Sand samples were labeled Bottom 1–7 and finally Top 1, with a total of eight samples.



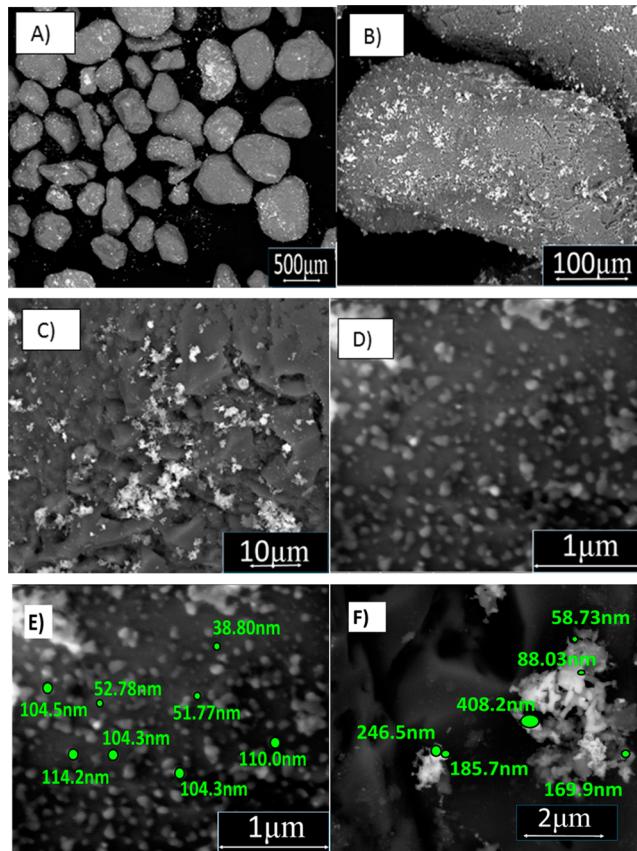
**Figure 2.** Metal content evolution in the liquid product during the catalyst deposition (MB: Mass Balance).

The sand calcination is performed at 500 °C in an air atmosphere for 12 h; during this process, all of the hydrocarbons are burnt and removed from the sand. During the SEM analysis, sands appeared clean, and no presence of hydrocarbons was observed in any case.

The approach taken for the SEM analysis was to measure as many particles in each of the samples as could be reasonably performed during the machine time allocated (a few hours); all measured particles were confirmed as catalyst by EDX analysis under focus. The presence of W or Mo was used as a definitive indicator of the presence of a catalyst particle, because the natural amount of these metals in the bitumen is very small. The sole presence of Ni was not considered as a catalyst particle due to its significant presence in the feed bitumen, which potentially produced nickel particle deposits. However, the occurrence of that seems not to take place as per our results.

As mentioned before, the measurement of a reasonably large number of particles was intended, as well as the determination of the catalyst particle size range. Figure 3 shows a series of photos taken with different zooms for the case of the Bottom 1 sample. Similar imaging was made for each of the sand samples. Figure 3A is a general overview of the sand sample, the grains presenting a nonuniform coating of bright material; contrary to what might be thought, not all of the bright material is catalyst. Figure 3B shows a focus on one particular sand grain with abundant presence of the bright material, while Figure 3C is a closer look at one region of the same grain. Looking closer in that region, discrete particles appear, as shown in Figure 3D. At this level with the EDX, particles may be identified if containing the metals of interest. Once the particles of interest are identified, they are measured (and labeled) with a ruler tool incorporated in the SEM software, as shown in Figure 3E. In many cases, particles were found grouped in small clusters, shown in Figure 3F. As a result, attempts were made to measure these particles individually whenever possible, in as many different grains and various locations on a grain as could be managed.

In general, it was found that catalyst particles are spherical and look like bright spots. Although this appearance may be used as a first approximation as to where to look for catalyst particles, it is by no means a fixed rule; therefore, EDX analysis remains an important tool. Figure 4 shows the EDX analysis performed in one specific area of a sand grain from the Bottom 2 sample. On this grain five spots were analyzed, three particles and two backgrounds as reference. EDX for points 1 (background) and 5 (catalyst particle) are shown in Figure 4, where the difference in the signals is quite evident. Point 1



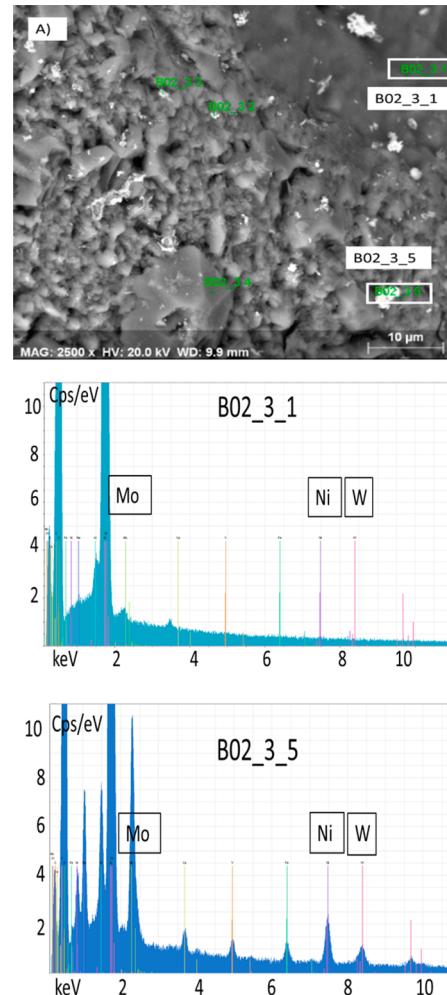
**Figure 3.** SEM imaging for sand sample Bottom 1 (0 cm). (A) Grains view. (B) Single grain. (C) Zoom on a particular zone of the grain. (D) Particle identification image. (E) Particle identification with labeling of catalyst particle sizes. (F) Cluster with individual particles labeled (Bottom 5).

shows no presence of either of the catalyst metals contrary to point 5 where Ni, Mo, and W signals are significant. The EDX analysis was performed in every one of the particles measured.

As we moved along the different samples further up on the reactor, the sand grains were much cleaner and catalyst particles were harder to find, as well as the presence of individual particles over the grains was much scarcer and they tended to be found in small clusters or groups. Figure 5 shows examples of this at different positions in the reactor. Among the identified particles, it was noticed that the presence of smaller particles (40–80 nm) is rarely found as we advanced to the top of the reactor, while particles between 100 and 400 nm were found all along the reactor.

In total 127 particles were measured averaging a size of 142 nm. It was also observed that the average particle size increases along the reactor. Table 2 shows the number and size of particles measured at the different heights of the reactor with the average for each sample. The smallest particle measured was around 39 nm and the largest is 1046 nm. The particle sizes showed in the SEM images are obtained using a ruler tool incorporated in the SEM software. The tool allows one to go to higher magnifications to properly look at the edges of the particle and then places the annotated value.

One of the disadvantages from single particle techniques is precisely the number of particles to investigate. The SEM detailed analysis of each sand samples would involve taking overviews of the sample and then going grain-by-grain looking



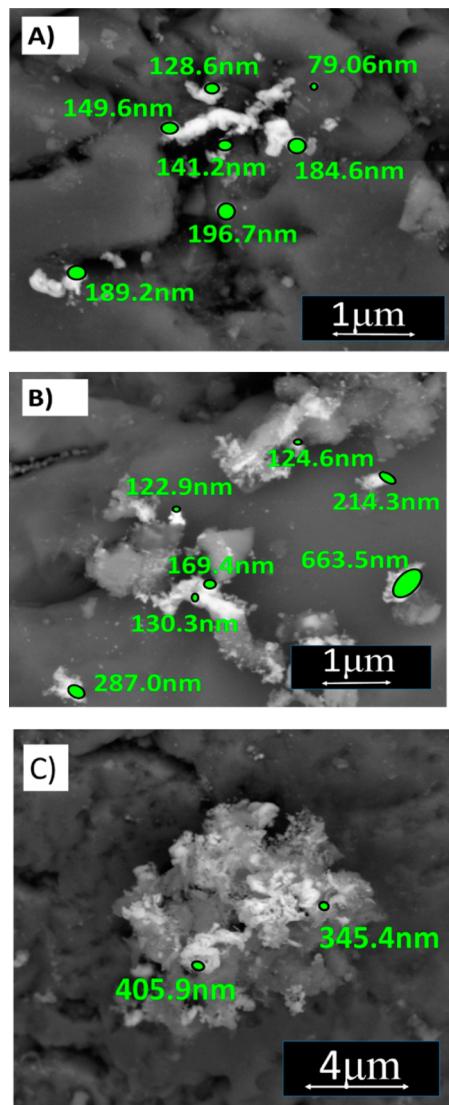
**Figure 4.** EDX analysis on spots on Bottom 2. (A) Spotted places of analysis. (B) Background EDX point 1 “B02\_3\_1”. (C) Catalyst particle EDX point 5 “B02\_3\_5”.

for particles and checking every different spot in every grain with a large amount of particles expected to be present, which may imply thousands of measurements. The reactor ( $L = 35$  cm and  $OD = 1$  in.) holds approximately 225 g of sand; therefore, it is unviable to look at a statistically representative number of sand grains. The amount of time and resources necessary to do so will make it impractical. This is one of the driving forces behind the investigation of different techniques to measure the ultradispersed catalyst particles.

The SEM was used as a qualitative reference to the particle size range encountered in the sample.

**3.3. NTA Adaptation to Sample Characteristics.** The use and operation of Nanosight NS300 is pretty simple and straightforward, as there are few parts that should be assembled and the sampling is easy to perform; however, there are several aspects and problems that were faced during the use of the equipment due to the particularities of the treated sample. This section addresses the troubleshooting of those problems. These observations are the result of many systematic trial and error procedures to obtain a good measurement with the NTA technique.

The NTA technology is principally used for aqueous samples, as reported in the literature, and to the knowledge of the authors there has been no published attempts to use this



**Figure 5.** Particle identification and size in different sand samples at different reactor depths. (A) Bottom 4. (B) Bottom 6. (C) Top 1.

technique for the analysis of hydrocarbon samples, especially bitumen or its heavy fractions. A short discussion of addressed points follows.

**Viscosity:** There is no specification for viscosity of the sample in the equipment; however, viscosities of 60 cP or higher already present challenges for properly filling the flow cell and restrict significantly the movement of the particles making tracking harder.

**Color:** The NanoSight NS300 has no restriction regarding sample color, but when dealing with dark samples they might be thick enough to prevent the laser from going through the

sample. This has to be managed through dilution to make possible the measurement. An initial dilution of 1/20 has been found to work.

**Presence of initial particles:** Sample with no catalyst and the solvent have to be analyzed initially to ensure that they have no or very few particles that will interfere with the catalyst particle determination. In case of the presence of particles, the settings to view and measure should be noted; if they are similar to the ones for the catalyst measurements, there might be interference. For the case of toluene and bitumen, the initial presence of particles is very scarce, requiring much more sensitive settings of the system as compared to those used for catalyst measurements. The most important settings are the camera level and threshold. Settings may vary between samples; however, in general we have found that for pure solvents (i.e., toluene) high camera levels up to 15 are required with low threshold levels of 3–4 (high sensitivity to center identification); bitumen requires camera levels around 11–12 and a threshold of 5–6; samples containing catalyst need lower camera levels of 8–9 with a higher threshold of 10–12.

**Dilution level:** The dilution level is important not only to control the viscosity and color of the sample but also to ensure an appropriate amount of particles in the camera sight. Too many particles can cause severe interference, while too few particles may not be representative of the sample, both of which can lead to misguiding results.

**Sample drift:** The presence of a general sample drift was found to enhance the detection and tracking of the particles for the bitumen sample. This has no effect on the final result because the NTA3.0 software recognizes the nonrandom movement and subtracts it before fitting the particle movement to the Stokes–Einstein equation. The sample drift allows one to measure more particles; however, large velocities should be avoided to guarantee particles are in sight for enough time.

**Length of the video:** Longer videos allow more particles to be tracked. Videos of 1 min were found to be most suitable for the type of samples used in this work. The time of the video is not the tracking time, which is referred to each particle, that is measured by the equipment for each particle it senses and statistically processed via the software. The length of the video allows more particles to be included in the analysis, but has no relationship to the Stokes–Einstein equation or tracking time.

**The “falling” particle phenomenon:** Another challenging phenomenon observed was the “falling” of particles that were in sight, a movement that did not appear to be random. Movement in the z-direction is not expected in a sample chamber with a thickness of 0.5 mm and therefore raises the concern of particle settling; this phenomenon was observed primarily in samples with low dilutions and disappeared at higher dilutions. Samples in which this occurred reported a very small particle size, because larger “falling” particles did not stay in the camera sight long enough to be tracked and measured.

**Table 2. Number and Size of Particles in the Sand Samples Taken along the Length of the Reactor As Determined by Analysis with SEM-EDX**

	Bottom 1	Bottom 2	Bottom 3	Bottom 4	Bottom 5	Bottom 6	Bottom 7	Top 1
distance from entrance (cm)	0	5	10	15	20	25	30	35
no. of particles measured	41	16	19	14	12	12	11	2
average	85	89	100	157	223	311	165	376
total particle				127				
overall average				142				

The falling may suggest settling of large particles; when analyzing the results, this aspect has to be considered to see if it really has an impact on the measurement.

**3.4. Nanoparticle Tracking Analysis (NTA) Results.** A total of seven samples were prepared starting with the lowest possible dilution up to a dilution at which there were no sufficient particles in sight to perform an accurate measurement. Table S3 presents the name, dilution level, and approximate catalyst concentration (ppm, by weight) of each sample. Figure 6 gives a visual image of the samples starting from the right with F1–F7 on the left.

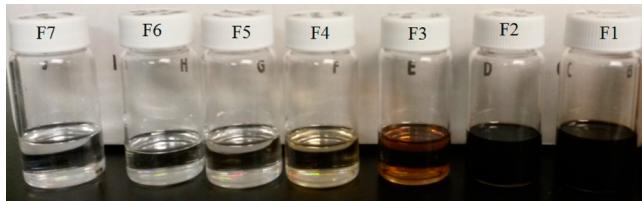


Figure 6. NTA sample appearance from F1 (right) to F7 (left).

On the basis of the sample appearance, F1 and F2 would not be able to be measured by DLS, while F3 may be on the limit of the DLS range.

The viscosity was measured for the first three samples (F1–F3) obtaining a value of 0.6 cP at room temperature (25 °C), which was very close to the viscosity of toluene (0.59 cP at 20 °C), and this value was used in every case. Regarding the appearance of the samples, they are essentially toluene because the amount of bitumen used in the preparation is very small, 0.5 g of bitumen in 9.5 g of toluene for F1. The samples were prepared and measured the same day, then left standing for 5 days at room temperature. After this period, another aliquot was taken from the top of each sample without any agitation and analyzed again. A visual inspection of these flasks was also performed, with no sedimentation of particles noted in any of them. A total of 10 videos were taken for each sample.

Samples F5, F6, and F7 had very few particles in the camera sight throughout the entire analysis, although the measurement was performed both days, so they are discarded to avoid misleading results.

F1 showed a couple of the previously discussed problems: in the first place, the high concentration of particles caused overlapping and poor tracking of the particles. As well, the “falling” phenomenon was abundantly present in the sample, and thus particles did not remain in sight for enough time to be tracked and sized. Both of these problems caused a tendency toward lower particle size because those particles that remained long enough to be tracked were the smallest ones. Figure 7 shows the merged results for this sample for both days.

The results show a very monodispersed sample with very small particles, but with a bigger diameter after 5 days. These results give some insight regarding the influence of the “falling” phenomenon on the results. If this phenomenon actually is referred to a settling process, the particles measured on day 5 could not be larger by any means than the ones measured on day 1. It seems that when the falling phenomenon is present only the smallest particles are able to be tracked properly. The F1 sample, although it is not good for the particle size characterization due to the high concentration and presence of the falling phenomenon, aids in understanding the impact of

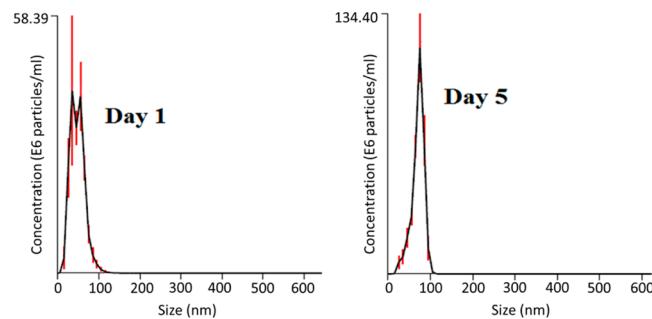


Figure 7. NTA merged results for F1 particle size measurement.

some of the unconventional phenomena happening due to the characteristics of the sample treated.

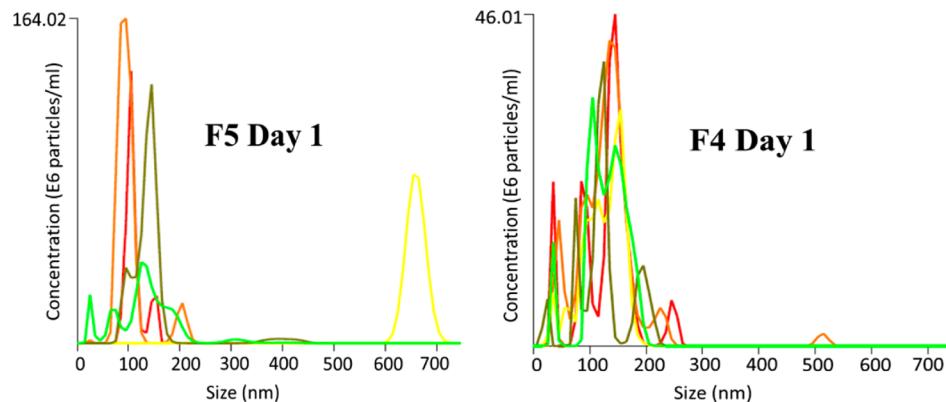
When analyzing sample F2, the amount of particles on sight was abundant but not overwhelming as in F1; the falling phenomenon was limited to a few particles in each video. However, the data collection and analysis was generally proper, with long particle tracking. Samples F3 and F4 showed a good amount of particles in sight and tracked well during all of the videos with no significant appearance of falling particles. Therefore, the result of the NTA will be focused on these three samples (F2, F3, and F4), and the technique will be assessed on the basis of these results.

It is important to mention, at this point, that a set of data (five videos) is considered good or valid by inspection and comparison of each of the individual video results; that is, the results have to show a certain level of agreement. A total agreement or overlapping of the peaks is not expected because the particles measured in each video are different. On the other hand, the particle diameters measured in each video are not expected to be radically different. A measurement will not be considered if, for example, video 1 shows diameters of 60 nm, video 2 at 300 nm, video 3 at 100 nm, etc. It is expected that all videos show peaks in the range of 20–70 nm, 100–130 nm, 200–300 nm, etc., because distinct may be indicative of sample inhomogeneity or another problem. This behavior was observed in samples F5, F6, and F7 where due to the small amount of particles tracked each video was significantly different from the others. Conversely, samples F2, F3, and F4 show a high overlap among individual results. Figure 8 shows an example of the previous discussion.

Figure 9 shows the merged results for samples F2, F3, and F4 for both days, and the results are summarized in Table S4 for each of the cases. Results are shown in terms of mean, mode, standard deviation (SD), D<sub>10</sub> (10% of particles under this value), D<sub>50</sub> (50% of particles with diameters under this measure), and D<sub>90</sub> (90% of particles below this diameter size).

The NTA shows particle diameters in the same range as those estimated via SEM. Modes are between 90 and 132 nm, and in general the means and modes are close, with the equipment detecting particles in the expected range from the small particles (35 nm) to the largest one (500, 600, and 1000 nm); see Table S4. We will discuss in detail each aspect of these results.

Comparing results of the same sample during different days, it was observed that all three samples show results in the same range on both days. Samples F2 and F3 show modes slightly higher for day 5; however, they are still in the same range of particles found with the SEM analysis. The cause for a higher particle size could be the result of some agglomeration within the sample or simply that the aliquot taken contained particles a



**Figure 8.** Agreement among videos in a sample. (A) F5 day 1, results differ strongly among individual videos. (B) F4 day 1, high overlapping between each video result.

little larger; because the values are in the same range, agglomeration does not seem to have a considerable effect.

In all cases, the NTA identified most particles as being in the range of 45–200 nm, but also identified particles in the 300, 400, 500, 600, and even the 900 nm range (Figure 9); these larger particles are present in smaller quantities, and the NanoSight could resolve and measure them, when present. An important observation to highlight is the importance of the incorporation of the sample drift and the proper length for each video, because when large particles show up they can hide the smaller ones present in the sample and then point toward a misleading direction; with the presence of drift, large particles are measured but come in and exit the camera range, and can be properly monitored in the total sample. The presence of particles even in small amounts such as in sample F3-day 5, can drive the mean value to a higher range, so this is a good example of why the mode is a preferred measure for the particle size.

Sample modes and means were in the range of 90–130 nm for all cases (except for F3, day 5, where the mean is higher due to the presence of large particles). By looking at the standard deviations (SD), it was observed that the values vary between 40 and 47 nm, showing that in general the distributions of the particle sizes in the sample are similar. Values of D<sub>10</sub>, D<sub>50</sub>, and D<sub>90</sub> serve to identify the range of sizes in which most of the particles are found and to weight the presence, proportion, and importance of outsider particle sizes. Looking at the D<sub>10</sub> results, only 10% of the particles are smaller than 65 nm in general (57 nm on average), while the same proportion of particles is found to be larger than 176 nm (D<sub>90</sub> values). Our results therefore indicate that 80% of catalyst particles are produced in the range of 65–180 nm, which varies slightly in each sample. The greatest amount of particles was found in the middle of this range, since the mode was 90–130 nm.

By comparing the results obtained from each sample, it was noticed that the F3 and F4 results match very well, whereas F2 has a tendency toward smaller particles, although still within the same range. This result is in accordance with the previous discussion regarding the dilution level of the sample and the falling phenomenon encountered while taking the measurements. Sample F2 had some presence of the falling particle phenomenon, and this may account for the slightly smaller particle diameter, similar to how sample F1 showed particle diameters of 50 nm. However, dilution levels in F3 and F4 show no difference among them.

The calculated error by the NTA 3.0 software can reach values of 15 nm in some cases, which is relatively high. However, due to the characteristics of the sample, it is not considered important, and with further development of the methodology (dilution level, sample preparation, sample drift, etc.), it is expected that errors in the measurement will be reduced.

**3.5. Technique Comparison.** The use of NTA technology for particle size measurement of dispersed catalyst in bitumen or heavy oil fractions as intended for the first time required the comparison with another technique to validate the obtained results to ensure their pertinence and also validate the use of the NTA technique. The deposition of catalyst particles on a sand pack at mild conditions was selected as a manner of freezing them to be able to observe and analyze the particles using SEM-EDX.

The SEM-EDX identified particles varied in size from 40 to 1046 nm with an average size of 142 nm, based on a total of 127 particles measured at different heights along the sand reactor. The NTA data through various samples and repeated measurements identified particles from 40 to 945 nm, with an average mean value of 122.5 and 111.3 nm as the mode value. Consequently, it may be affirmed that both techniques identified particle sizes in the same range, so the NTA did not leave any particle without measuring. The average value obtained by NTA is slightly lower than that measured by SEM; however, it is not possible to consider the SEM average representative of the entire population due to the intrinsic nature of the analysis, but even after these considerations the mean value is found in the same range of particle diameter.

The NTA analysis indicates that around 80% of the particles measured are between 57 and 176 nm, with 10% under 57 nm and 10% above 176 nm. Looking at the SEM data collected, 15% (19 particles) are found to be smaller than 57 nm and 19% (24 particles) above 176 nm, values that are higher in both cases, but help to confirm the accuracy of the NTA analysis for the determination of the sizes of particles dispersed in bitumen.

#### 4. CONCLUSIONS

A method and procedure has been developed to use NTA technology for the particle size measurement of dispersed submicrometer size catalyst particles in bitumen and heavy oil fractions, consisting basically of dilution of the sample to adjust viscosity, color, and particle concentration to the capacities of the equipment (NanoSight NS 300).

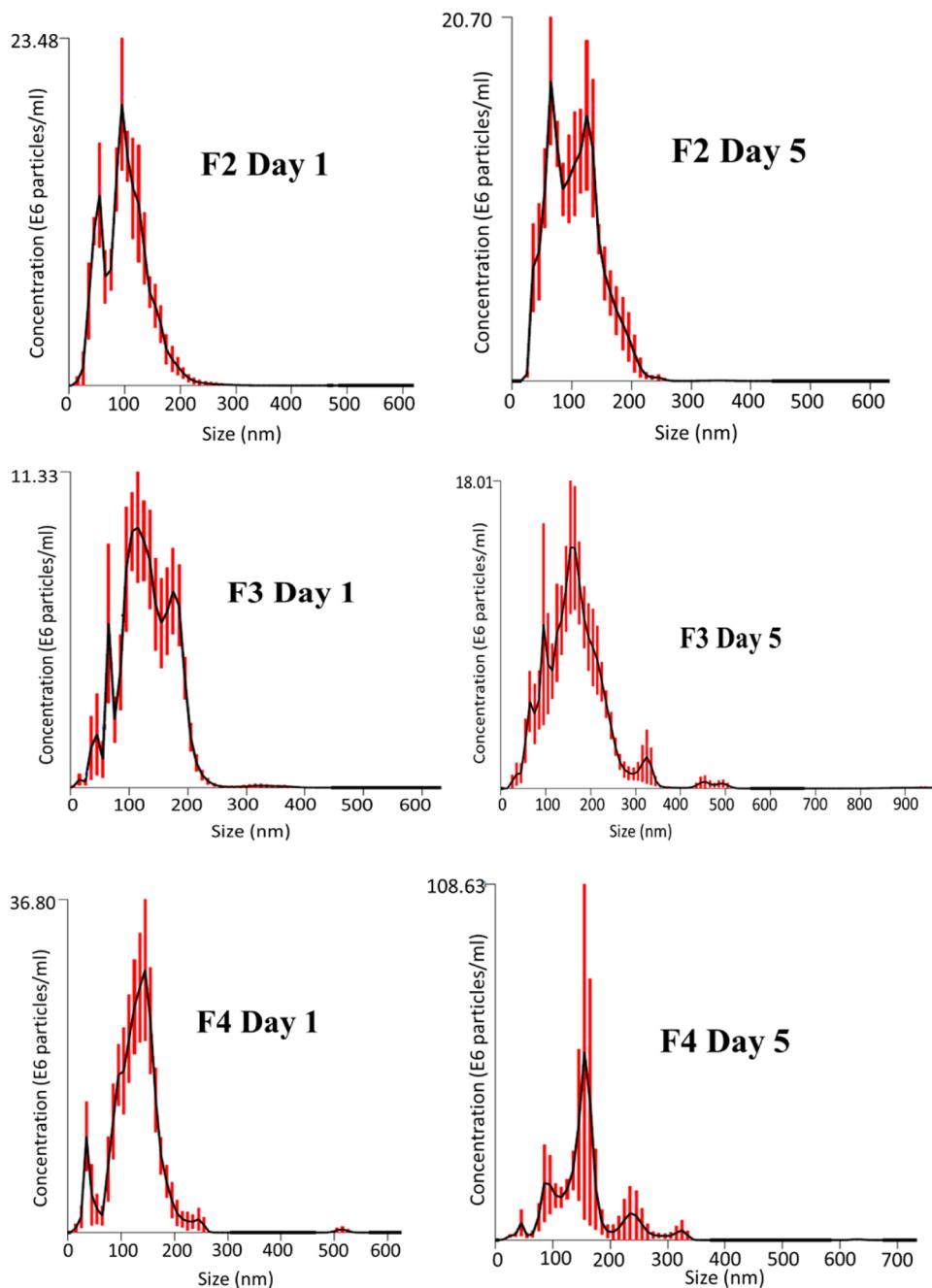


Figure 9. Quantitative particle size analysis. Merged results for samples F2, F3, and F4 for both days.

NTA results compared to particle sizes determined by SEM-EDX of the same catalytic dispersions “anchored” on sand show particles in the size range between 40 and 1000 nm. Average particle sizes are in the same range but show around a 16% difference on value.

The particle size was successfully measured by NTA obtaining an average diameter of 111 nm (mode), with 80% of the particles having sizes between 57 nm (D<sub>10</sub>) and 176 nm (D<sub>90</sub>).

Adequate procedures were developed to cope with factors such as sample color, viscosity, and the presence of initial particles. Best practices to improve the measurement are proposed regarding dilution level, length of measurement, and incorporation of sample drift for submicrometer particles dispersed in bitumen, and a solution was proposed for most

of the cases. It was found that some other issues, such as the “falling particle phenomenon”, which could not be procedurally established, seemed not to have a significant effect on the measurement observed.

Most intermediate handling steps that cause uncertainty in the particle size determination were successfully overcome during this detailed application of the NTA technology to the uncommon system of mineral particles suspended in a dense, viscous, and dark media. This work has found the NTA to be a fast, reliable, and acceptably accurate technique to measure particle size in the nanometer and submicrometer scale for bitumen and heavy oil fractions as the suspending media, taking advantage of the combination of single and ensemble particle measurements of the technique.

## ■ ASSOCIATED CONTENT

### § Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.iecr.5b02420](https://doi.org/10.1021/acs.iecr.5b02420).

Tables for liquid product distribution (Table S1), metal content in liquid products (Table S2), NTA sample dilutions and concentration (Table S3), and NTA merged result values (Table S4) ([PDF](#))

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [vmrodrig@ucalgary.ca](mailto:vmrodrig@ucalgary.ca).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC), Nexen-CNOOC Ltd., and Alberta Innovates-Energy and Environment Solutions (AIEES) for the financial support provided through the NSERC/NEXEN/AIEES Industrial Research Chair in Catalysis for Bitumen Upgrading. Also, the contribution of facilities from the Canada Foundation for Innovation, the Institute for Sustainable Energy, Environment and Economy, the Schulich School of Engineering, and the Faculty of Science at the University of Calgary is greatly appreciated. We especially thank Dr. Chris DeBuhr of the Department of Geoscience at University of Calgary for his valuable help with the SEM-EDX data acquisition, imaging, and analysis.

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