Engineering Ni-Mo-S Nanoparticles for Hydrodesulfurization

Bodin, Anders; Christoffersen, Ann-Louise N.; Elkjær, Christian F.; Brorson, Michael; Kibsgaard, Jakob; Helveg, Stig; Chorkendorff, Ib

Published in:
Nano Letters

Link to article, DOI:
[10.1021/acs.nanolett.8b00472](https://doi.org/10.1021/acs.nanolett.8b00472)

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Bodin, A., Christoffersen, A-L. N., Elkjær, C. F., Brorson, M., Kibsgaard, J., Helveg, S., & Chorkendorff, I. (2018). Engineering Ni-Mo-S Nanoparticles for Hydrodesulfurization. *Nano Letters*, 18(6), 3454-3460. <https://doi.org/10.1021/acs.nanolett.8b00472>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Engineering Ni-Mo-S Nanoparticles for Hydrodesulfurization

Anders Bodin [1], Ann-Louise N. Christoffersen [1], Christian F. Elkjær [2], Michael Brorson [2], Jakob Kibsgaard [1], Stig Helveg [2], Ib. Chorkendorff* [1]

[1] Department of Physics, Technical University of Denmark, Fysikvej, Building 312, DK-2800 Kgs. Lyngby, Denmark

[2] Haldor Topsøe A/S, Haldor Topsøes Allé 1, DK-2800 Kgs. Lyngby, Denmark

* Corresponding author - email: ibchork@fysik.dtu.dk

Abstract

Nanoparticle engineering for catalytic applications requires both a synthesis technique for production of well-defined nanoparticles as well as measurements of their catalytic performance. In this paper, we present a new approach to rationally engineering highly active Ni-Mo-S nanoparticle catalysts for hydrodesulfurization (HDS), i.e. removal of sulfur from fossil fuels. Nanoparticle catalysts are synthesized by sputtering of a $\text{Mo}_{75}\text{Ni}_{25}$ metal target in a reactive atmosphere of Ar and H_2S , followed by gas aggregation of the sputtered material into nanoparticles. The nanoparticles are filtered by a quadrupole mass filter and subsequently deposited on a planar substrate, such as a grid for electron microscopy or a microreactor. By varying the mass of the deposited nanoparticles, it is demonstrated that the Ni-Mo-S nanoparticles can be tuned into fullerene-like particles, flat-lying platelets and up-right oriented platelets. The nanoparticle morphologies provide different abundances of Ni-Mo-S edge sites, which are commonly considered as the catalytically important sites. Using a micro-reactor system, we assess the catalytic activity of the Ni-Mo-S nanoparticles for HDS of dibenzothiophene. The measurements show that platelets are twice as active as the fullerene-like particles, demonstrating that the Ni-Mo-S edges are more active than basal planes for the HDS. Furthermore, the up-right standing orientation of platelets show an activity that is six times higher than the fullerene-like particles, demonstrating the importance of the edge sites number and accessibility to reduce e.g. sterical hindrance for the reacting molecules.

Keywords: *Catalysis, hydrodesulfurization (HDS), reactive gas-aggregation, nanoparticles, nano-engineering, MoS_2*

Introduction

The functional behaviour of nanometer-sized particles depends on their shape and surface structure and the structure-function relationship is generally difficult to predict. To advance the understanding of the structure-function relationship it is beneficial to investigate nanoparticles having a narrow shape distribution. Well-defined ensembles of nanoparticles can be synthesized by e.g. gas aggregation. Although synthesis by gas aggregation is a well-known methodology,^{1–5} much of the literature is focussed on gas aggregation in inert atmosphere. Recently, Ni–MoS₂ nanoparticles have been synthesized by sputtering of Ni and MoS₂ targets in an inert atmosphere.⁶ Syntheses in reactive atmospheres such as e.g. oxygen,^{7–10} nitrogen,¹¹ and H₂S¹² have also been investigated, but most of these studies focus on the synthesis itself rather than technological applications of the nanoparticles. In this paper we combine gas aggregation synthesis of Ni-Mo-S nanoparticles with examinations of their catalytic performance for hydrodesulfurization (HDS).

HDS is the process of removing sulfur impurities from organosulfur compounds in mineral oil distillates. The HDS process involves reaction of the organosulfur compounds with hydrogen over a suitable catalyst, typically molybdenum sulfide promoted with nickel or cobalt.^{13,14} The HDS process has gained considerably attention through the past four decades due to environmental concerns regarding the emission of sulfur dioxide SO₂ from the combustion of fossil fuels, which have led to increasingly strict regulations on the sulfur content in refined fuels. For example, the limit for sulfur in diesel in the European Union has decreased from 500 ppm in 1996 to 10 ppm in 2009.^{15,16} This leads to significant technological challenges in developing better HDS catalysts.

The active sites for HDS catalysis are generally considered to be the edges of the MoS₂ nanoparticles with edge-attached Ni or Co in the so-called "Ni-Mo-S" or "Co-Mo-S" phase.¹⁷ Currently, it is challenging to reach the sub-10 ppm levels of sulfur because of very refractory sulfur-containing molecules in the feedstocks, such as dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT).¹³ This is often attributed to the remaining sulfur being embedded in the molecular structure thereby leading to sterical hindrance in binding S to the active sites on the catalyst surface. To improve the accessibility to the Ni-Mo-S and Co-Mo-S edge sites requires improved control over the shape and orientation of the catalyst nanoparticles. Although sterical hindrance has been much debated, e.g.,^{18–23} the effect is difficult to discern in industrial catalysts because the catalyst nanoparticles formed by wet synthesis procedures typically are present with wide distributions of shapes and orientations. We present a new approach to engineering a more homogeneous ensemble of catalyst nanoparticles with controlled shapes and orientations and thereby address the role of sterical hindrance and the importance of Ni-Mo-S edge-sites for HDS catalysis, particularly HDS of DBT. Our nanoparticle synthesis approach is based on aggregation of sputtered Mo and Ni in a reactive atmosphere of H₂S and Ar, filtering in a quadrupole mass filter and subsequent post-annealing in H₂S. This synthesis method can only produce small amounts of nanoparticles ($\sim 500 \frac{\text{ng}}{\text{cm}^2}$ per hour of deposition), and is therefore not scalable to industrial production rates. Rather, it can create nanoparticle model systems to establish structure/activity relations, and thus provide a tool for finding highly active nanoparticle morphologies that can later be synthesized by scalable methods.

We supplement the catalytic measurements by extensive characterization of the nanoparticles by scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). Finally, the observed particle structures are correlated to their catalytic activity.

The small amount of catalytic nanoparticles necessitates the use of a very small reactor volume to detect the products of the catalytic reaction. We utilize a micro-reactor platform of our own design for this purpose citeHenriksen2009,Andersen2012,Christoffersen2018. The

conditions (e.g. mass transport, pressure, temperature, etc.) in such a reactor are different from those in an industrial HDS reactor, and our experiments are therefore designed to show a general trend in the relation between structure and catalytic activity rather than comparisons with literature values. The micro-reactor platform thus enables the use of our nanoengineered nanoparticles in gas-phase catalysis experiments which would otherwise have been impossible.

Experimental Methods

Ni-Mo-S nanoparticle model systems were synthesized in a ultra-high vacuum (UHV) nanoparticle source (Nanogen50 model, Mantis Deposition LTD) by magnetron sputtering, gas aggregation and mass-filtering as illustrated in Figure 1. A $\text{Mo}_{75}\text{Ni}_{25}$ metal target was sputtered in an atmosphere of Ar (~ 0.1 mbar) and H_2S ($\sim 5 \times 10^{-3}$ mbar), after which the sputtered material aggregated into nanoparticles in the gas phase in a differentially pumped "aggregation zone". See SI for detailed synthesis parameters. After aggregation, the particles underwent a supersonic expansion through an aperture, and subsequently they did not grow further. A significant fraction of the particles were negatively charged,³ and could therefore be filtered according to their mass-to-charge ratio ($\frac{m}{z}$) in a quadrupole mass-filter (QMF, MesoQ model, Mantis Depositions LTD) with a mass resolution of $\frac{m}{\Delta m} = 20$. Nanoparticles were deposited with the two mass-to-charge ratios of $\frac{m}{z} = \frac{200 \text{ kamu}}{-1e}$ and $\frac{m}{z} = \frac{440 \text{ kamu}}{-1e}$. The particles can potentially carry multiple elementary charges, but are referred to as 200 kamu and 440 kamu in the following for easier notation, where kamu is 1000 atomic mass units. The particles were deposited in the unsealed reaction chamber of a micro-reactor for subsequent catalytic testing, and the nanoparticle loading was accurately determined by integrating the electric deposition current on the micro-reactor. The nanoparticle beam was rastered with an X-Y lens system during deposition to ensure homogeneous deposition on the reactor area. Nanoparticles were

Figure 1: Synthesis procedure for Ni-Mo-S nanoparticles A $\text{Mo}_{75}\text{Ni}_{25}$ target is magnetron sputtered in a gaseous mixture of Ar and H_2S . The sputtered material aggregates into nanoparticles which are filtered according to their mass-to-charge ratio in a quadrupole mass-filter and deposited on a micro-reactor for catalytic testing.

also deposited on two types of substrates for transmission electron microscopy: (i) 20 nm SiO₂ thin film grids (same material as the SiO₂ micro-reactors) and (ii) lacey carbon/Cu grids with added agglomerates of graphene. The graphene provided an ultra-low background for high resolution imaging of MoS₂ crystals.²⁴

As a reference, metallic Ni-Mo nanoparticles with a mass-to-charge ratio of $\frac{m}{z} = \frac{134\text{kamu}}{-1e}$ (referred to as 134kamu) were synthesized without H₂S in the gas mixture. This mass was chosen since the metal content in these particles is close to that of 200 kamu Ni-Mo-S particles. Some of the metallic particles were produced in another nanoparticle source (Nano-Beam 2011, Birmingham Instruments, described in e.g.^{25,26}) and mass filtered in a lateral time-of-flight mass filter with the same mass resolution of $\frac{m}{\Delta m} = 20$.²⁷ The synthesis principles are identical in the two setups, and the use of a different setup should not influence the results.

After deposition of nanoparticles, the contents of the micro-reactors were exposed to air before they were sealed with a pyrex lid by an anodic bonding process.²⁸ To ensure that the sulfidic nanoparticles were fully sulfided in spite of exposure to atmospheric air, they were heated to 350 °C in 10 % H₂S/90 % H₂ at 1000 mbar for an hour in the reactors before activity tests. Both in-flight sulfided Ni-Mo-S nanoparticles and metallic Ni-Mo nanoparticles were exposed to this post-sulfidation treatment, and "Ni-Mo-S" and "Ni-Mo" thus refer to the state of the particles during deposition onto the micro-reactor.

In order to investigate the effect of the post-sulfidation treatment, SiO₂ TEM grids with metallic Ni-Mo nanoparticles of 134kamu and in-flight sulfided Ni-Mo-S nanoparticles of 200kamu were heated in a tube furnace to 350 °C in 10 % H₂S/90 % H₂ at 1000 mbar for an hour. After this treatment, they were imaged with STEM, just as the other nanoparticles.

After deposition of nanoparticles, the micro-reactors were transferred to an adjacent UHV-chamber without air exposure and characterized with X-ray photoelectron spectroscopy (XPS) using Mg K_α radiation generated in a SPECS RQ 20/38 X-ray gun and a single-channel Phoibos 100 SCD hemispherical energy analyzer for photoelectron detection. For detailed XPS analysis, 200 kamu Ni-Mo-S nanoparticles were deposited on a micro-reactor at a higher loading ($850 \frac{\text{ng}}{\text{cm}^2}$) in order to maximize the photoelectron signal. A reference spectrum was obtained on a single crystal MoS₂ sample from SPI Supplies.

The size, shape and element composition of the nanoparticles were examined using electron microscopy. The size and shape of the nanoparticles were investigated using a FEI Titan Analytical 80-300ST transmission electron microscope equipped with an aberration-corrector for the objective probe forming lens. The microscope was operated in the scanning transmission electron microscopy (STEM) mode at a primary electron energy of 300 keV, with a probe size below ca. 1 Å and with a probe current of 1 – 2 nA. STEM images were acquired in the high-angle annular dark-field (HAADF) mode.

The elemental composition of the nanoparticles was examined using a FEI Talos transmission electron microscope equipped with the ChemiSTEM energy-dispersive X-ray (EDX) detector system. The microscope was operated in STEM mode at a primary electron energy of 200 keV with a probe size of ca. 3 Å and a probe current of 700 pA. STEM images were acquired simultaneously with EDX spectra of in-flight sulfided Ni-Mo-S nanoparticle deposited at a mass of 200 kamu on a graphene-loaded Cu/lacey carbon TEM grid. Typical acquisition times were 5-10 minutes for maps of 123 nm × 123 nm with 512 pixels × 512 pixels. Elemental maps were generated pixel-by-pixel from the measured peak intensity of the Mo L and Ni K lines without background subtraction. After acquisition the maps were treated by a 2D average filter. The MoL_α peak intensity convolutes a contribution from the SK_α line, meaning that the red color in the elemental maps represents the combined Mo and S intensity and the green color is the Ni intensity.

The catalytic activity of the nanoparticles was assessed by the use of a micro-reactor platform that has been described in detail elsewhere.²⁹⁻³¹ In short, the reactor consisted of a micro-fabricated Si chip with a reactor volume of ~ 250 nL connected to a time-of-flight mass

spectrometer through a capillary outlet, allowing on-line monitoring of the gas composition in the reactor volume. Reactant gases were dosed through flow-controllers to two inlet channels, and the pressure in the reactor was controlled with a back-pressure controller. The flow through the reactor was $\sim 5 \times 10^{14}$ molecules/s corresponding to a short residence time of $\sim 6 - 7$ s. The reactor was heated with resistive heaters patterned on the backside of the chip, and the temperature was measured with a k-type thermocouple mounted on the front of the reactor.

DBT is a solid at room temperature, and it was therefore dosed by sublimation when He was flowed over heated DBT crystals at 110°C . The entire test setup including tubing, micro-reactor, etc., was heated to the same temperature to avoid DBT condensation in cold spots. The He + DBT flow was set to 2 SCCM and the H_2 flow to 1 SCCM; the pressure in the reactor was set to 800 mbar, corresponding to partial pressures of ~ 533 mbar He, ~ 266 mbar H_2 , and ~ 0.4 mbar DBT.

Results and Discussion

Figure 2 shows HAADF STEM images of 134kamu metallic Mo-Ni and 200kamu in-flight sulfided Ni-Mo-S nanoparticles (subpanels **a**) and **b**), revealing a significant difference in morphology and particle sizes. Whereas the metallic particles have spherical

Figure 2: Low-magnification STEM images, size-distributions and elemental map from EDX: **a)** Metallic Ni-Mo nanoparticles deposited with target mass 134 kamu; **b)** In-flight sulfided Ni-Mo-S nanoparticles deposited at a target mass of 200 kamu. Both images were obtained on SiO_2 TEM grids. **d)** and **e)** Histograms of particle diameters from Ni-Mo and Ni-Mo-S particles, respectively. The diameters were calculated as average diameters from the projected particle area. **c)** Elemental map of Mo+S and Ni obtained with EDX. **f)** Volume distribution of the 200 kamu Ni-Mo-S nanoparticles, showing that the particle histogram has clear peaks corresponding to 200 kamu, 400 kamu, 600 kamu, and 800 kamu.

shapes and appear as homogeneous bright dots, the in-flight sulfided particles have more irregular morphologies with either a uniform contrast or patches of different contrast levels. A significant number of particles exhibit flat and plate-like morphologies, and some show faceting corresponding to a hexagonal lattice, resulting in hexagonal or triangular features. This is all consistent with the layered crystal structure of MoS₂ and findings on wet-synthesized industrial Co-Mo-S catalysts.³² The high surface-area shapes of the particles are due to the reactive H₂S passivating undercoordinated metal atoms during particle growth, diminishing the driving force towards low surface-area spheres. The difference between metallic and in-flight-sulfided nanoparticles is clearly visible in the size-distribution histograms (subpanels **d**) and **e**)), which show average diameters calculated from the projected particle area (see SI for more information). The metallic nanoparticles have an average diameter of $d = 4.0 \pm 0.3$ nm (0.3 nm is the standard deviation), whereas the in-flight-sulfided particles have $d = 9.0 \pm 2.1$ nm.

Although the projected area is a good measure of particle size, it does not take the contrast of the particles into account. In fact the in-flight sulfided particles with patches of different contrast levels could be due to different thickness or composition as the HAADF-STEM contrast scales with the total projected atomic number roughly as $Z^{1.7}$. Therefore, another size-distribution of the Ni-Mo-S sample was made by weighting the pixels of the nanoparticles with their background-subtracted intensity, effectively resulting in a particle volume distribution (see SI for details). Surprisingly, the particle volume histogram, Figure 3 **f**), shows not only particles with a mass of 200 kamu, but also 400 kamu, 600 kamu, and 800 kamu particles. This finding is consistent with co-deposition of a significant amount of multiple charge/multiple mass particles along with the single charge/single mass particles. Integration of the histogram peaks reveals that 40 % is $\frac{1m}{1e}$, 35 % is $\frac{2m}{2e}$, 16 % is $\frac{3m}{3e}$, and 10 % is $\frac{\geq 4m}{\geq 4e}$, where the percentages reflect the number of particles.

The presence of multiple masses is the main reason for the much broader size-distribution in Figure 2 **e**). It should be noted that a certain mass-deviation will translate into a larger spread in particle diameter for plate-shaped particles than spherical particles since the particle mass scales with d^3 for a spherical particle and only d^2 for a platelet, but this is likely a smaller effect. There is no indication of multiple mass/charge particles in the metallic sample, which matches previous experience in our group for metallic depositions where only $\frac{2m}{2e}$ particles are sometimes observed.²⁶ It is possible that the Ni-Mo-S particles can conserve more charge due to the poor electrical conductivity between layers in MoS₂-type semiconductors,³³ but it is also possible that the co-deposition of multiple charge/multiple mass particles is simply due to a broader distribution of particle masses exiting the aggregation zone in case of the Ni-Mo-S particles.

XPS quantification, based on areas of the spectral peaks weighted with the relevant sensitivity-factors, show that the in-flight sulfided Ni-Mo-S nanoparticles are partly sulfided, with a stoichiometry of Mo_{0.8}Ni_{0.2}S_{1.1}. This partial sulfidation is also reflected in the binding energy of the Mo3d_{5/2} peak (228.2 eV), which is in-between that of metallic Ni-Mo (227.5 eV) and the MoS₂ reference (228.8 eV). Since the particles are partially sulfided and in a non-equilibrium state, it is likely that Mo is present in a range of oxidation states from Mo(0) as in metallic Mo to Mo(IV) as in MoS₂; this is reflected in broadening of the Mo3d peaks. The Ni2p_{3/2} peak shifts to higher binding energies in Ni-Mo-S (853.2 eV) as compared to Ni-Mo (852.5 eV), indicating at least partial sulfidation. See SI for XPS spectra and details.

Figure 2 **c**) shows an elemental map acquired with EDX; since the most intense Mo and S peaks (MoL_α and SK_α) overlaps, the red color in the map represents both Mo and S. XPS already showed that the Mo is sulfided, and EDX was thus applied to show the position of Ni in the molybdenum sulfide. The elemental map shows that Ni, Mo and S are present in the same particles, rather than e.g. forming separate Ni-S and Mo-S particles. Based on the

Figure 3: High-resolution STEM images and deposition mass profiles of the Ni-Mo-S nanoparticles a) Ni-Mo-S nanoparticles deposited at a target mass of 200 kamu on graphene. The particles in the white square are magnified in b), by obtaining a new image with a smaller step-size. Here, the atomic structure is clearly visible as evidenced and the Fourier transform in the inset which shows a spatial periodicity of $1/2.7 \text{ \AA}^{-1}$ matching that of MoS_2 (100), corresponding to flat-lying MoS_2 platelets on the substrate. d) and e) show images of Ni-Mo-S particles deposited at a target mass of 440 kamu on graphene. The Fourier transform inset in e) reveals a (001) periodicity as well, corresponding to co-existing upright-oriented platelets (marked stripe structure) within the same nanoparticle. c) and f) show the mass profiles for of the nanoparticles exiting the aggregation zone before mass filtering for the 200 kamu and 440 kamu depositions, respectively. Note that the particles are negatively charged, resulting in negative current.

present results, it can not be excluded that regions are partly enriched or depleted in Ni, which would to some extent lead to broadening in the volume distribution in Figure 2 f). However, based on the results from Zhu et al.,³⁴ the Ni preferentially attach at the edges and is thus most likely distributed around the edges of the nanoparticles. For nanoparticles containing multiple layers of MoS_2 with different terminations, the Ni could be distributed along with these terminations, smearing out of the Ni-signal. In summary, although the Ni-doped edges cannot clearly be distinguished in the EDX maps, the abundance of Ni in the particles make it very likely that catalytically active Ni-Mo-S edge terminations are present in the nanoparticles.

Figure 3 a) shows a high-resolution STEM image of 200 kamu Ni-Mo-S nanoparticles on a graphene substrate. A fast Fourier transform (FFT) of a magnified STEM image obtained with a smaller step-size, Figure 3 b), shows reciprocal lattice spots at $1/2.7 \text{ \AA}^{-1}$, corresponding

to (100) lattice planes of MoS₂.²⁴ Thus the Ni-Mo-S particles of the 200 kamu sample appears to form planar sheets having with the basal plane oriented along the substrate. As for the nanoparticles on SiO₂, the Ni-Mo-S structures have either triangular, hexagonal or irregular shapes with a uniform contrast or patches of different contrast levels. Figure 3 c) shows the mass spectrum of the nanoparticles exiting the aggregation zone before deposition and the target mass that was chosen for deposition shown as a dotted line. As the particles are negatively charged, a negative current is generated.

We attempted to shift the particle synthesis towards the highest possible masses, which resulted in the mass spectrum in Figure 3 f). Although the current increases and moves towards higher masses, the current maximum is still located close to 200 kamu, suggesting that the apparatus has a preference towards the production of particles with this mass. Particles were deposited at 440 kamu since this gave a good compromise between high mass and high deposition current. The resulting particles can be seen in Figure 3 d), which reveals a significant change in morphology. The 440 kamu particles in general have higher contrast than the 200 kamu particles under the same illumination conditions, indicating that they are thicker. Their shape is also rather irregular. Moreover, the magnified image in Figure 3 e), obtained with a smaller step-size, shows regions of two different lattice spacings. The FFT, shown as an inset, reveals reciprocal lattice spots at $1/2.7 \text{ \AA}^{-1}$, corresponding to the (100) lattice planes, as well as $1/6.7 \text{ \AA}^{-1}$, corresponding to the (001) lattice planes of MoS₂.³⁵ That is, the 440 kamu Ni-Mo-S nanoparticles consist of regions of MoS₂ oriented along the substrate surface as well as regions of MoS₂ oriented upright from the substrate surface. Thus, a synthesis method for creation of nanoparticles with exposed basal plane edges was established.

The effect of post-sulfiding nanoparticles can be seen in Figure 4, which shows STEM images of metallic and in-flight-sulfided nanoparticles on SiO₂ TEM grids after post-sulfidation.

The in-flight sulfided nanoparticles (a) and b)) retain their plate-like structure during the post-sulfidation treatment, and still resemble Figure 2 b). Fourier transforms of the image (not shown) reveals that the MoS₂ (100) periodicity is present, confirming that the MoS₂ basal plane is still exposed. Since the in-flight-sulfided Ni-Mo-S particles of 200 kamu retain their structure during post-sulfidation, the same is likely to be the case for the 440 kamu Ni-Mo-S particles.

The metallic particles shown in Figure 4 c) and d), on the other hand, undergo a drastic change from uniform spherical shapes (Figure 2 a)) to layered, fullerene-like molybdenum sulfide structures.^{36,37} Fourier transforms of the image reveals both MoS₂ (100) and (001) periodicities, where the latter are clearly visible in the image. The structures do not seem to expose many edge terminations; rather, the MoS₂ layers are covering the particles in morphologies similar to those previously observed by e.g. Wang et al.³⁸ Apart from the sulfidation, the particles have also sintered, which is likely due to the metallic particles having a larger driving force for sintering than the in-flight-sulfided particles, which are passivated by sulfur and do not significantly lower their surface energy by sintering.

In all experiments with hydrodesulfurization of DBT, biphenyl (BiPhe) was observed as the reaction product. In order to quantify the catalytic activity of the nanoparticle samples, we define the mass activity as

$$\text{Mass Activity} \left[\frac{\text{molecules}}{\text{s ng}} \right] = \frac{\dot{N}_{DBT}}{m_{\text{metal}}} \times \text{Conversion}, \quad (1)$$

where $\dot{N}_{DBT}$ is the flow of DBT entering the reactor in molecules/s (see SI), m_{metal} is the mass of metal (Ni+Mo) in the catalyst, and conversion is defined as

$$\text{Conversion} = \frac{S \times A_{\text{BiPhe}}}{S \times A_{\text{BiPhe}} + A_{\text{DBT}}}, \quad (2)$$

Figure 4: Effect of post-sulfidation of the nanoparticles: a) and b) STEM images of in-flight-sulfided nanoparticles of 200 kamu after post-sulfidation, showing that the particles retained their plate-like morphology. c) and d) Nanoparticles deposited as 134 kamu metallic Ni-Mo after post-sulfidation, where they have become sintered, fullerene-like sulfide-structures.

where A is a raw integrated mass spectrum peak area and S is a relative sensitivity factor that accounts for the different ionization cross-sections of BiPhe and DBT in the mass spectrometer. S has earlier been found to be 1.3 on the setup.³¹

Three microreactors with different types of nanoparticles were compared: one reactor with metallic Ni-Mo particles (134 kamu), one with in-flight sulfided Ni-Mo-S particles with exposed basal planes (200 kamu), and one with in-flight sulfided Ni-Mo-S particles with exposed edges (440 kamu). The mass loadings in the reactors were ~ 75 ng metal (Ni+Mo) in the metallic Ni-Mo and 440 kamu Ni-Mo-S particle samples; the 200 kamu Ni-Mo-S particle sample had a loading of ~ 375 ng metal. The differences in mass loading is accounted for by the mass normalization in our definition of mass activity.

Figure 5 shows the mass activity of the three reactors at 245 °C. A clear trend is visible in the catalytic activity: The metallic Ni-Mo particles are the least active, the basal plane-exposing Ni-Mo-S particles are ~ 2 times as active, and the edge-exposing Ni-Mo-S particles are ~ 6 times as active. The trend that the edge-exposing Ni-Mo-S nanoparticles are the most catalytically active is in good agreement with the well-established fact that the active sites of Ni-Mo-S catalysts for HDS are the nanoparticle edges.^{14,39–42}

Figure 5: Hydrodesulfurization activity of three different types of nanoparticle samples: metallic Ni-Mo particles (134 kamu), in-flight sulfided Ni-Mo-S particles with exposed basal planes (200 kamu), and in-flight sulfided Ni-Mo-S particles with exposed edges (440 kamu).

Conclusion

In conclusion, we have presented a novel method for synthesizing Ni-Mo-S nanoparticles by sputtering, reactive gas aggregation and mass filtering, and shown that the synthesized particles are active for hydrodesulfurization of dibenzothiophene. By nanoengineering the structure of the in-flight sulfided Ni-Mo-S nanoparticles, we have increased the mass activity six-fold compared to fullerene-like particles produced by post-sulfiding metallic nanoparticles. The results underline the importance of maximizing edge-exposure of molybdenum sulfide HDS catalysts when desiring to circumvent e.g. sterical hinderance. To the best of our knowledge, this paper is the first report of Ni-Mo-S nanoparticles synthesized by reactive gas aggregation, and thus paves the way for a new approach to engineering highly active HDS catalysts.

Supporting Information Available:

Detailed nanoparticle synthesis parameters, methodology for determining particle diameter and volume distributions, X-ray photoelectron spectra and analysis, definition of mass activity.

Acknowledgements

This work was supported by the Danish Research Council - Technology and Production through the research grant HYDECAT.

References

- [1] Yatsuya, S.; Kamakura, T.; Yamauchi, K.; Mihama, K. *Jpn. J. Appl. Phys.* **1986**, *25*, L42–L44.
- [2] Hahn, H.; Averbach, R. S. *J. Appl. Phys.* **1990**, *67*, 1113–1115.
- [3] Haberland, H.; Karrais, M.; Mall, M.; Thurner, Y. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **1992**, *10*, 3266–3271.
- [4] Pratontep, S.; Carroll, S. J.; Xirouchaki, C.; Streun, M.; Palmer, R. E. *Rev. Sci. Instrum.* **2005**, *76*.
- [5] Kolipaka, L.; Vajda, S. In *Gas-Phase Synth. Nanoparticles*; Huttel, Y., Ed.; Wiley-VCH Verlag GmbH, 2017; pp 243–268.
- [6] Escalera-Lopez, D.; Niu, Y.; Yin, J.; Cooke, K.; Rees, N. V.; Palmer, R. E. *ACS Catal.* **2016**, *6*, 6008–6017.
- [7] Hihara, T.; Peng, D.-L.; Sumiyama, K. *Mater. Trans.* **2001**, *42*, 1480–1484.
- [8] Ahadi, A. M.; Zaporajtchenko, V.; Peter, T.; Polonskyi, O.; Strunskus, T.; Faupel, F. *J. Nanoparticle Res.* **2013**, *15*.
- [9] Gonzalez, J. A.; Andres, J. P.; De Toro, J. A.; Muniz, P.; Munoz, T.; Crisan, O.; Binns, C.; Riveiro, J. M. *J. Nanoparticle Res.* **2009**, *11*, 2105–2111.
- [10] Marek, A.; Valter, J.; Kadlec, S.; Vyskočil, J. *Surf. Coatings Technol.* **2011**, *205*, 573–576.
- [11] Peter, T.; Polonskyi, O.; Gojdka, B.; Mohammad Ahadi, A.; Strunskus, T.; Zaporajtchenko, V.; Biederman, H.; Faupel, F. *J. Appl. Phys.* **2012**, *112*, 1–7.
- [12] Majeski, M. W.; Bolotin, I. L.; Hanley, L. *ACS Appl. Mater. Interfaces* **2014**, *6*, 12901–12908.
- [13] Bensch, W. In *Compr. Inorg. Chem. II Second Ed. From Elem. to Appl.*, 2nd ed.; Reedijk, J., Poeppelmeier, K. R., Eds.; Elsevier Ltd., 2013; Vol. 7; pp 287–321.
- [14] Topsøe, H.; Clausen, B. S.; Massoth, F. E. *Hydrotreating Catalysis Science and Technology*; Springer Verlag, 1996.
- [15] European Committee for Standardization, European Standard EN 590:2009 - Automotive fuels - Diesel - Requirements and test methods. 2009.
- [16] www.dieselnet.com/standards/eu/fuel.php - accessed on 2018-04-05.
- [17] Topsøe, H.; Clausen, B. S.; Canida, R.; Wivel, C.; Mørup, S. *J. Catal.* **1981**, *68*, 433–452.
- [18] Houalla, M.; Broderick, D. H.; Sapre, A. V.; Nag, N. K.; de Beer, V. H. J.; Gates, B. C.; Kwart, H. *J. Catal.* **1980**, *61*, 523–527.
- [19] Hayden, T. F.; Dumesic, J. A. *J. Catal.* **1987**, *103*, 366–384.
- [20] Sakashita, Y.; Araki, Y.; Honna, K.; Shimada, H. *Appl. Catal. A* **2000**, *197*, 247–253.
- [21] Shimada, H. *Catal. Today* **2003**, *86*, 17–29.
- [22] Arrouvel, C.; Breyse, M.; Toulhoat, H.; Raybaud, P. *J. Catal.* **2005**, *232*, 161–178.

- [23] Costa, D.; Arrouvel, C.; Breysse, M.; Toulhoat, H.; Raybaud, P. *J. Catal.* **2007**, *246*, 325–343.
- [24] Hansen, L. P.; Ramasse, Q. M.; Kisielowski, C.; Brorson, M.; Johnson, E.; Topsøe, H.; Helveg, S. *Angew. Chemie - Int. Ed.* **2011**, *50*, 10153–10156.
- [25] Hernandez-Fernandez, P.; Masini, F.; McCarthy, D. N.; Strebel, C. E.; Friebel, D.; Deiana, D.; Malacrida, P.; Nierhoff, A.; Bodin, A.; Wise, A. M.; Nielsen, J. H.; Hansen, T. W.; Nilsson, A.; Stephens, I. E. L.; Chorkendorff, I. *Nat. Chem.* **2014**, *6*, 732–738.
- [26] Masini, F.; Hernández-Fernández, P.; Deiana, D.; Strebel, C. E.; McCarthy, D. N.; Bodin, A.; Malacrida, P.; Stephens, I.; Chorkendorff, I. *Phys. Chem. Chem. Phys.* **2014**, *16*, 26506–26513.
- [27] von Issendorff, B.; Palmer, R. E. *Rev. Sci. Instrum.* **1999**, *70*, 4497–4501.
- [28] Vesborg, P. C. K.; Olsen, J. L.; Henriksen, T. R.; Chorkendorff, I.; Hansen, O. *Chem. Eng. J.* **2010**, *160*, 738–741.
- [29] Henriksen, T. R.; Olsen, J. L.; Vesborg, P.; Chorkendorff, I.; Hansen, O. *Rev. Sci. Instrum.* **2009**, *80*.
- [30] Andersen, T.; Jensen, R.; Christensen, M. K.; Pedersen, T.; Hansen, O.; Chorkendorff, I. *Rev. Sci. Instrum.* **2012**, *83*.
- [31] Christoffersen, A.; Bodin, A.; Elkjær, C.; Sørensen, J.; Kibsgaard, J.; Chorkendorff, I. *J. Phys. Chem.* **2018**, *122*, 1699–1705.
- [32] Baubet, B.; Girleanu, M.; Gay, A. S.; Taleb, A. L.; Moreaud, M.; Wahl, F.; Delattre, V.; Devers, E.; Hugon, A.; Ersen, O.; Afanasiev, P.; Raybaud, P. *ACS Catal.* **2016**, *6*, 1081–1092.
- [33] Evans, B. L.; Young, P. A. *Proc. R. Soc. A* **1965**, *284*, 402–422.
- [34] Zhu, Y.; Ramasse, Q. M.; Brorson, M.; Moses, P. G.; Hansen, L. P.; Topsøe, H.; Kisielowski, C. F.; Helveg, S. *Catal. Today* **2016**, *261*, 75–81.
- [35] Lu, Y.; Yao, X.; Yin, J.; Peng, G.; Cui, P.; Xu, X. *RSC Adv.* **2015**, *5*, 7938–7943.
- [36] Margulis, L.; Salitra, G.; Tenne, R.; Talianker, M. *Nature* **1993**, *365*, 113–114.
- [37] Feldman, Y.; Wasserman, E.; Srolovitz, D. J.; Tenne, R. **1995**, *267*, 222–225.
- [38] Wang, H.; Zhang, Q.; Yao, H.; Liang, Z.; Lee, H. W.; Hsu, P. C.; Zheng, G.; Cui, Y. *Nano Lett.* **2014**, *14*, 7138–7144.
- [39] Lauritsen, J. V.; Bollinger, M. V.; Lægsgaard, E.; Jacobsen, K. W.; Nørskov, J. K.; Clausen, B. S.; Topsøe, H.; Besenbacher, F. *J. Catal.* **2004**, *221*, 510–522.
- [40] Kibsgaard, J.; Lauritsen, J. V.; Laegsgaard, E.; Clausen, B. S.; Topsoe, H.; Besenbacher, F. *J. Am. Chem. Soc.* **2006**, *128*, 13950–13958.
- [41] Bollinger, M. V.; Jacobsen, K. W.; Nørskov, J. K. *Phys. Rev. B* **2003**, *67*.
- [42] Helveg, S.; Lauritsen, J.; Laegsgaard, E.; Stensgaard, I.; Norskov, J.; Clausen, B.; Topsøe, H.; Besenbacher, F. *Phys. Rev. Lett.* **2000**, *84*, 951–4.