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Synthesis, characterization and environmental assessment of nanosized MoS_2 particles for lubricants applications

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HIGHLIGHTS

- The wet chemical synthesis of Molybdenum Sulfide nanoparticles has been investigated.
- The synthesis parameters and the ratio of reactants have been optimized.
- Softly agglomerated and amorphous nanoparticles with a mean size of 30 nm have been fully characterized.
- A LCA has been conducted to analyze the environmental impacts of nano-manufacturing.

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ABSTRACT

Molybdenum sulfide nanoparticles have been successfully obtained, for lubricant applications, by means of a wet chemical synthesis in an aqueous solution employing ammonium molybdate, citric acid and ammonium sulfide as the reactants. Some molybdenum-citrate complexes were formed and they reacted with the ammonium sulfide to form MoS_2 nanoparticles. Mo:citrate molar ratio was identified as being the most relevant of the synthesis parameters that affected the phase and morphology of the final products. The optimized nanoparticles were softly agglomerated and amorphous, with a mean size of the primary particles of about 50 nm. A Life Cycle Assessment (LCA) has been conducted since an early process design phase to analyze the environmental performance of nano-manufacturing. This supplied necessary background Life Cycle Inventory (LCI) data for a better understanding of the direct and indirect environmental gains that MoS_2 nanoparticles will transfer to the final product, i.e. the fully formulated oil and its subsequent end-use.

1. Introduction

Fluid lubricants are used in almost every field of human technological activity and their purpose is multi-fold: they reduce frictional resistance, protect the contacting surfaces of engines against wear, remove wear debris, reduce heat and contribute to cooling, improve fuel economy and improve emissions.

Advanced nanomaterials have shown some promise because of their contribution to reducing friction and enhancing protection against wear [1–3].

When incorporated in full lubricant formulations in a stable way, and if their performance benefits can be sustained under those circumstances, nanomaterials offer the possibility of some performance breakthroughs which have not witnessed since the development of the now ubiquitous anti-wear additives, Zinc Dialkyl Dithiophosphates (ZDDP's), about 70 years ago. These developments can contribute to a substantial energy saving, reduce equipment maintenance and lengthen the life of the machines. In the case of engine oil (crankcase) applications, these nanomaterials can help increase the durability and performance of exhaust-treatments and reduce harmful emissions: in fact, exhaust catalysts tend to become poisoned by the Sulphur and Phosphorous that are present in conventional lubricant additives.

Transition metal dichalcogenides, with the generic formula MX_2 (M = W, Mo; X = S, Se), whose synthesis was first demonstrated at the Weizmann institute by Tenne and co-workers [4–6], seem to be very promising materials to be dispersed as nanoparticles in the oil matrix. They involve a reaction between MO_3 and H_2S, in reducing atmosphere at high temperatures, and the corresponding sulphide (WS_2 or MoS_2) is obtained. Many other synthetic routes have also been followed to obtain these kinds of nano-structured materials [7–16].

In terms of sustainable development, nanotechnologies are expected to open the way towards new engineering solutions, and nano-based products are often associated with presumably

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revolutionary performance in terms of resource efficiency or environmental care, including human health [17].

However, in order to fully understand the environmental benefits that nanotechnologies will transfer to end-products/services, incorporation of life cycle thinking is warmly recommended since the initial process design stage [18]. This should lead to the development of competitive, safe, and environmentally responsible engineering and commercialization of nano-products [19].

It is well known that nanotechnologies are heavily energy and resource intensive in the manufacturing phase, and that the overall resource use and environmental impact per mass unit of nanocomponent can be huge [18–21]. However, it is commonly pointed out that the nanocomponent is only a fraction of the end-product, implying that only a small fraction of the environmental impact can be attributed to the nanocomponent and its manufacture. Therefore, an assumption is often made that the nanocomponent's contribution is negligible. This may be true if the functional unit, i.e., the basis of the study, is set at a single end-product [20]; however, it has to be proved and quantified by means of a sound and scientifically accepted methodology, and in a life-cycle perspective.

Despite the great interest on life cycle impacts of nanotechnologies [22,23], there is still limited quantitative information on energy and resource intensity of nanocomponents manufacturing, especially for what it concerns inorganic nanomaterials synthesis and subsequent processing [20,24]. Som et al. [23] argue, in fact, that there is an urgent need in obtaining datasets about the most important nanotechnological processes and publishing these datasets in well-known databases. At the same time, there is also an urgent need to develop a consistent, transparent and meaningful methodological approach for conducting Life Cycle Assessments (LCAs) of engineered nanomaterials, by identifying what needs to be measured as outputs, and how the impacts can be assessed in an impact assessment. There is in fact still some confusion in conducting environmental assessment of nanotechnologies, and the term "Life Cycle Assessment" is often misunderstood as equivalent to "life cycle thinking" [23]. Life cycle thinking is a general approach, which implies that the environmental assessment should cover the whole life cycle, while the wording "Life Cycle Assessment" stands for a well identified methodological framework. LCA was developed in the early 1990s and that is described in the ISO 14040/14044 standards [25,26] and in the guidelines that were recently issued by the Joint Research Centre of the European Commission [27]. Although the overall framework of LCA is flexible and comprehensive enough to embrace environmental assessment of nanotechnologies, there is still a lot to do before LCA can be considered fully operational to business in that sector.

The present study focuses on the synthesis of MoS_2 nanoparticles which have to be incorporated in engine lubricant oils. A wet synthesis technique has been devised. This technique is based on the preparation of an aqueous solution of citric acid and ammonium molybdate to form a complex of molybdenum(IV) with citric acid, to which a suitable amount of ammonium sulphide was added to obtain MoS_2. This technique resorts to a simple and scalable process, and involves low-cost reagents, instead of other more complex reaction methods. Moreover, LCA is used to identify and quantify the from-cradle-to-gate energy use and environmental impacts associated with the new synthesis process.

2. Experimental procedure

2.1. Synthesis and characterization

The synthesis of the nanostructured MoS_2 powders was carried out by means of a new modified version of the procedure described by Aridi and Al-Daous [28]. We exploited and optimized the amount of citric acid as reductant/complexing agent with the aim to obtain MoS_2 nanoparticles with controlled particles size as detailed in the paragraph 3.1. The reactants were ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, citric acid $C_6H_8O_7$ and ammonium sulfide $(NH_4)_2S$, all of which were supplied by Sigma Aldrich. An aqueous solution was prepared by dissolving suitable amounts of ammonium molybdate and citric acid in distilled water in order to obtain the following Mo:citrate molar ratio: 1:1, 1:2 and 1:4. The quantity of citric acid employed in the synthesis was considered as the significant parameter and it was varied to 4 times the stoichiometric value. The solution was kept at 90 °C and the pH was adjusted to 4 by adding a suitable quantity of ammonium hydroxide. After the complete dissolution of the reactants, 3.75 ml of a 20 wt% solution of ammonium sulfide in water was added drop-by-drop. The solution changed from clear to dark red, and finally to black. The solution was subsequently centrifuged at 4000 rpm for 1 h, and the obtained precipitates were washed in distilled water three times and then dried at 80 °C for 12 h. The powders were calcined at 900 °C for 1 h in flowing Ar.

The products were characterized by X-ray diffraction (X'Pert Philips, range 2θ: 10÷70°, radiation Cu Kα, λ = 1.54056 Å), X-ray fluorescence (Rigaku ZSX100E) and by X-ray photoelectron spectroscopy with a VG Escalab 200-C X-ray photoelectron spectrometer and a non monochromatic Mg Kα source. A pass energy of 20 eV, a resolution of 1.1 eV, and a step of 0.2 eV were used for high-resolution spectra. The effects of sample charging by referring the spectral line shift to the C 1s binding energy value of 284.6 eV were eliminated. The microstructural characterization was carried out by means of field emission scanning electron microscopy (Leo Supra 40) equipped with an EDS probe and transmission electron microscopy (JEOL JEM 2010). The samples were prepared for electron microscopy observations by suspending some products in isopropanol, through ultrasonic mixing, for half an hour, and subsequently by placing a drop of the dispersion on a copper grid coated with a layer of amorphous carbon.

2.2. Life cycle thinking applied to nanotechnologies

With focus on the synthesis process, a from-cradle-to-gate LCA was conducted using the SimaPro 7 software [29]. Inventory data for reactants and electricity supply were obtained from the Ecoinvent database [30] and the functional unit was set at 1 g of MoS_2 nanoparticles.

Given that the new synthesis process is expected to remarkably reduce primary energy consumption and greenhouse emissions, the analysis is focused on two indicators: cumulative energy demand (CED) and greenhouse emissions (GWP100), according to the characterization factors reported in Frischknecht and Jungbluth [34].

It must be remarked that previous examples of synthesis of MoS_2 nanoparticles with an inorganic Fullerene-like structure are reported in the literature [31–33] and operate at a temperature of 900 °C, while the maximum temperature reached in the synthesis process described in this paper is 90 °C. However, the above mentioned literature references report no LCI data that would be necessary for a comprehensive environmental comparison.

3. Results and discussion

3.1. MoS_2 nanoparticles synthesis and characterization

The citric acid was considered to play a key role in the synthesis of the MoS_2 nanopowders due to its complexing behavior, which favoured the formation of a citrate-molybdenum complex [35], which reacts with the ammonium sulfide to produce the molybdenum