

Comparisons between naturally-occurring and chemically-produced (synthetic) molybdenum disulfide

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Naturally-occurring molybdenum disulfide is extracted from molybdenite ore. In its lubricant-grade fine powder form, as a dark grey or black solid, it is the molybdenum disulfide supplied and distributed by chemical suppliers for use as a lubricant either dry or in suspension in an oil or grease. In its coarser powder form molybdenum disulfide is the feedstock for roasting into technical grade molybdenum trioxide.

Naturally-occurring molybdenum disulfide

For natural molybdenum disulfide as used as a lubricant, the particle size depends on the grade (the extent of grinding). For example the Climax Molybdenum Technical Fine has particles of ca. 6 μm (finely ground) and the Technical grade (natural) ca. 30 μm (Yakov Epshteyn and Thomas J. Risdon, Molybdenum Disulfide In Lubricant Applications – A Review, Climax Molybdenum, presented at the 12th Lubricating Grease Conference, January 2010, Goa, India). The surface area of natural molybdenum disulfide of particle size 35 μm was $1 \text{ m}^2 \text{ g}^{-1}$ (www.specialchem4polymers.com/urw/lubricants-surface.aspx).

Supported chemically-produced (synthetic) molybdenum disulfide catalysts

Chemically-produced (synthetic) molybdenum disulfide as encountered in the catalyst industry is prepared by sulfiding molybdenum trioxide, i.e. heating the oxide in hydrogen sulfide or with an organic sulfur compound. Molybdenum disulfide-based catalysts are used in the hydrodesulfurisation of organic sulfur compounds in petroleum crudes. The molybdenum disulfide is supported on alumina. Cobalt or nickel is added as a catalyst promoter. The sulfided catalyst may be prepared *in situ*, i.e. by sulfiding a supported molybdenum trioxide precursor in the reactor or *ex situ*, i.e. by sulfiding the oxide catalyst precursor in a sulfiding reactor other than the reactor used in the hydrodesulfurisation process. The pre-sulfiding may be done at a different site. The sulfided catalyst will then be transported to the hydrodesulfurisation site. **The sulfided catalyst is air sensitive and kept/transported under an inert gas, nitrogen or argon, to avoid self-heating due to oxidation.**

Synthetic alumina-supported molybdenum disulfide catalysts have been much studied, for example by electron microscopy, to determine the composition and structure of the molybdenum sulfide component of the catalyst. The molybdenum sulfide component is the active part of the catalyst. It consists of slabs that are part of the molybdenum disulfide structure. The dispersion and morphology have been reviewed (H. Topsoe, B.S. Clausen and F.E. Massoth, *Hydrotreating Catalysis*, Springer 1996, pp. 88 seq.). The consensus is that the sulfided Mo/alumina catalysts consist of two-dimensional S-Mo-S layers, which are single slabs of the molybdenum disulfide structure, oriented parallel with the alumina surface. On a Mo/alumina catalyst with 10-15% molybdenum the lateral size of the domains is 1-1.5 nm (8 – 25 molybdenum atoms).

A more recent academic study of an alumina supported molybdenum disulfide catalyst (B. Pawelec, P. Castañoband, T.A. Zepeda, *Applied Surface Science*, 2008, 254, 4092–4102) agrees that the catalyst consists of molybdenum disulfide slabs but considers them to be edge-bonded to the alumina: “All sulfided samples exhibit mainly the edge-bonded molybdenum disulfide clusters oriented roughly parallel to the electron beam direction.” There were 4 stacking layers. The surface density of MoS₂ particles (MoS₂ particles/50 nm²) was ca. 2 to 3. The particle size was ca. 4.0 nm.

The specific BET surface area of the catalysts was ca. 700 m² gcat⁻¹ (for technical catalysts the surface area is ca. 250 m² gcat⁻¹).

Whatever the detailed structure of the supported synthetic molybdenum disulfide catalysts we can conclude that the molybdenum disulfide is in the form of slabs or particles of no more than ca. 4 nm diameter.

Unsupported chemically-produced (synthetic) molybdenum disulfide catalysts

Unsupported synthetic molybdenum disulfide catalysts are also encountered. They are prepared, for example, by sulfiding unsupported molybdenum trioxide or by thermal decomposition of ammonium tetrathiomolybdate. The unsupported synthetic molybdenum disulfide catalysts are often used in basic research (for example, to study the catalytic properties of molybdenum disulfide without a support) and in some technical processes in suspension in a heavy oil.

Typical properties of unsupported synthetic molybdenum disulfide catalysts are these (C. Calais, N. Matsubayashi, C. Geantet, Y. Yoshimura, H. Shimada, A. Nishijima, M. Lacroix and M. Breyse, Journal of Catalysis, 1998, 174, 130–141): The specific surface areas varied from 4 to 125 m² gcat⁻¹ depending on the method of preparation. The particle size by EXAFS was close to 1 nm and by TEM 3 to 4 nm.

The surface area of a synthetic molybdenum disulfide was 67 m² gcat⁻¹ compared with a value of 3.3 m² g⁻¹ for a commercial (natural) molybdenum disulfide (C.H. Amberg in P. C.H. Mitchell (ed.), Chemistry and Uses of Molybdenum, Proceedings of the Climax First International Conference, Reading UK, 1973, p. 181).

Molybdenum disulfide oxidation

Quote from the paper of Epshteyn and Risdon (op. cit.): “The oxidation characteristics of lubricant grade natural molybdenum disulfide have been studied by several researchers. The thermal oxidation rate of molybdenum disulfide in air studied by x-ray diffraction showed that below 300 °C, the rate is very slow and difficult to measure accurately, and that below 388 °C, Molybdenum disulfide oxidized at a slower rate than WS₂. The oxidation behaviour of Molybdenum disulfide in dry air has also been studied by thermo-gravimetric analysis. It was determined that 10%, 50% and 90% Molybdenum trioxide was formed at temperatures of 435 °C, 466 °C and 516 °C respectively. **Besides temperature and humidity, the molybdenum disulfide particle size can significantly affect the rate of oxidation. Smaller particles of molybdenum disulfide have much higher rate of oxidation compared to larger particles** due to the fact that edge sites of the particles oxidize at a much higher rate versus the basal plane area of a particle, and also, finely divided particles have a higher specific ratio of the edge to basal plane. “ H. E. Sliney, "Proceedings of USAF Aerospace Fluids and Lubricants Conf., April 1963, (350-367). P. M. Ku, ed. M. T. Lavik, T. M. Medved and G. D. Molybdenum trioxide, ASLE Trans 11, (1968), 44-55.

Conclusion

We can conclude that, although surface areas vary depending on the method of preparation, **the particle size (largest dimension) and surface area of chemically-produced(synthetic) molybdenum disulfide are always much greater than for natural molybdenum disulphide.** Here is a tabular comparison:

Property	Natural MoS ₂	Chemically-produced (synthetic) MoS ₂
Particle size	30,000 nm; 35,000 nm	1 to 1.5 nm; 3 to 4 nm
Surface area	1 m ² g ⁻¹ ; 3.3 m ² g ⁻¹	67 m ² gcat ⁻¹ ; 4 to 125 m ² gcat ⁻¹
Oxidation in air	No	Yes

Note: figures separated by “;” taken from different literature sources as cited in the text above