

# Made by molybdenum

Anders Lennartson muses on molybdenum and its essential role in catalysing reactions from the bacterial to the industrial scale.

The three minerals historically named galena, molybdena and plumbago have several common features — they are all soft, dark materials with a metallic lustre. Before the advent of modern chemical methods, these three substances were often mistaken for one another. Because galena (lead(II) sulfide) was known to be a useful lead ore, it was commonly believed that molybdena and plumbago also contained lead. However, molybdena (which we call molybdenite today) was actually molybdenum(IV) sulfide, and plumbago was what we now call graphite. This historical misunderstanding is why, even today, the graphite-clay mixture in pencils is often referred to as ‘lead’.

Needless to say, early attempts to produce lead from molybdena or plumbago invariably failed, and attention instead turned to further investigating the content of these minerals. In 1776, a small sample of molybdena was presented to Carl Wilhelm Scheele, a pharmacist in the small Swedish city of Köping. Aged just 33, Scheele had not only discovered hydrofluoric acid, chlorine, tartaric acid, arsenic acid and uric acid, but had also characterized the first manganese and barium compounds. If anyone was going to be able to sort out the confusion over these minerals, it was probably him.

The molybdena sample was indeed similar in appearance to the plumbago Scheele had in his shop, but still different enough to warrant further investigation. He asked his friends for more of this substance until he had acquired enough for a thorough chemical study. In the molybdena sample he found no lead, but what he did find came as a surprise; he was able to isolate<sup>1</sup> a previously unknown substance, molybdic acid ( $\text{MoO}_3 \cdot \text{H}_2\text{O}$ ). Once on the right track with molybdena, he also showed that plumbago was a form of carbon, but that’s another story altogether.



Reducing molybdic acid to molybdenum itself required more sophisticated equipment than a small pharmacy store could supply. Scheele turned to Peter Jacob Hjelm in Stockholm, who mixed molybdic acid with charcoal and linseed oil and heated it in an intense fire. After opening the sealed crucible he found the first sample of metallic molybdenum, in the form of small grains. Molybdenum metal produced in this way has a high carbon content, making it brittle and close to useless, and so throughout the nineteenth century it remained on the shelves of chemistry labs. In the early 1900s, methods of obtaining pure molybdenum in larger quantities were developed, enabling molybdenum steels to become increasingly important. These materials found their way into car frames and tools, and during the two world wars large amounts were also used for armour plating. More recently, molybdenum metal has been used as a target in X-ray tubes, both for medical applications and research purposes; Mo- $\text{K}_\alpha$  radiation is used extensively by crystallographers.

Not only is molybdenum useful in materials science, it is also very important in catalysis. Modern gasoline and diesel fuels have far less impact on the environment than they did a few decades ago because of the removal of sulfur from petroleum using molybdenum sulfide catalysts. Molybdenum-oxide-based catalysts are used by industrial chemists to selectively oxidize alcohols to aldehydes,

reactions that otherwise suffer from competing carboxylic acid formation. In 2005, Richard Schrock shared the Nobel Prize in Chemistry for the development of olefin metathesis catalysts, including those based on molybdenum carbenes.

The use of molybdenum compounds for catalysis was, however, not a discovery first made by man. Long before humans roamed the Earth, several crucial processes were already being catalysed by molybdenum-containing enzymes — and still are. One such process is the conversion of atmospheric nitrogen gas to ammonia. When this reaction is performed industrially, it requires temperatures above 300 °C and pressures of about 200 bar. In contrast, nitrogen-fixing bacteria living in symbiosis with certain plants carry out the same process under physiological conditions, by exploiting the power of nitrogenase enzymes. Most nitrogenases have a molybdenum atom in their active site, which consists of a cluster of seven iron atoms, nine sulfur atoms, one molybdenum atom capped by a homocitrate ligand, and a histidine residue.

Not only can some molybdenum enzymes reduce dinitrogen to ammonium ions, certain anaerobic microbes — so-called acetogens — use other molybdenum-containing enzymes to convert carbon dioxide and hydrogen to formate ions, and eventually to acetyl-coenzyme A. It has been estimated that these organisms produce around  $10^{11}$  tons of acetate from  $\text{CO}_2$  gas annually<sup>2</sup>. Put another way, our world would be quite different without molybdenum! □

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