# Oxidation of Sulfides to Sulfoxides and Sulfones with Hydrogen Peroxide

A. Lattanzi,[a] S. Meninno,[a] A. Parrella,[a] G. Brancatelli,[b] S. Geremia,[b] C. Gaeta,[a] C. Talotta[a] and P. Neri,[a]

[a] *Dipartimento di Chimica e Biologia, Università di Salerno, Via Giovanni Paolo II 132, 84084 Fisciano(Salerno), Italy*
[b] *Centro di Eccellenza in Biocristallografia, Dipartimento di Scienze Chimiche e Farmaceutiche, Universitàdi Trieste, via L. Giorgieri 1, 34127 Trieste, Italy*
E-mail: cgaeta@unisa.it

Polyoxometalates (POMs) are nano-sized, functional inorganic clusters with differentcompositions and structures, which have been applied in catalysis, medicine, and materialsscience.[1] Thanks to their rich redox chemistry, they demonstrated to be suitable catalysts foroxidations of alkenes, alcohols and sulfides.[2] Given the insolubility of POMs in many organicsolvents, a typical approach to enhance the scarce mass transfer between POMs and organicsubstrates has been based on exchange of the counterion with classical cation surfactants (e.g.tetrabutyl ammonium). Consequently, surfactant encapsulated POM complexes proved to bemore soluble and effective catalysts in oxidative processes. We have designed andcharacterized a polyoxomolybdate-calixarene hybrid[3] (tetra-ammonium-calix[4]arene·[Mo8O26]4-)**1** with a view to study its performance in oxidation reactions (Figure 1).

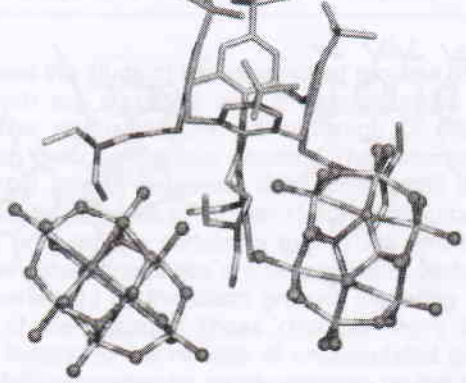

**Figure 1.** X-Ray structure of POM-calixarene hybrid **1**.The au consists of one tetracationic calixareneand two half of tetraanionic POM. A different Mo coordination is observed for the two centrosymmetricPOM structures: the left one with all octahedral Mo and the right one with two Mo in tetrahedral geometry.

The development of efficient, selective and environmentally friendly procedures of oxidation ofsulfides to sulfoxides and sulfones is a highly active research area,[4]due to the importance ofthese products as synthetic intermediates, in pharmaceutical and petroleum industry.Interestingly, we found that compound **1** served as one of the most efficient POM-basedcatalysts in the oxidation of sulfides either to sulfoxides or sulfones, when working at only 0.05%mol loading, using 30% H2O2 solution as the oxidant in acetonitrile.

[1] Special issue on "polyoxometalates", *Chem. Rev.* **1998**, *98*.
[2] Mizuno, N.; Kamata, K.; Yamaguchi, K. *Top. Catal.* **2010**, *53*, 876-893.
[3] For an example of polyoxotungstate-calixarene hybrid, see: Ishii, Y.; Takenaka, Y.; Konishi, K. *Angew.Chem. Int. Ed.* **2004**, *43*, 2702–2705.
[4] Lattanzi, A. in *Comprehensive Organic Synthesis* (2nd edition), (Eds. Knochel, P., Molander, G. A.),Oxford, Elsevier, **2014**, *7*, 837-879.