

# Zelite Encapsulated Molybdenum Sulfide Clusters Mimicking the Nitrogenase Enzyme's Active Site

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## Introduction

Transition metal sulfides (TMS) have a long-standing use as hydrodefunctionalization and hydrogenation catalysts for hydrotreating, but recently also gained major attention as photocatalysts and electrode materials.[1,2] In nature, TMS clusters act as building blocks for active sites of many enzymes, most noticeably of the nitrogenase and hydrogenase family.[3] Elucidating both the structure of the industrially applied, layered materials and that of enzyme active sites has been the focus of intensive studies.[1,3]

We synthesized well-defined molybdenum sulfide clusters within the confinement of a zeolite host adopting earlier recipes.[4] Using a multitude of state-of-the-art spectroscopic methods in close combination with theoretical calculations, we will illustrate, how these clusters encapsulated in zeolite pores mimic the geometric and electronic structures of TMS cluster-based cofactors in the pockets of enzymes.[5] These materials show distinctively different catalytic hydrogenation pathways compared to traditional layered MoS<sub>2</sub>.

## Materials and Methods

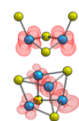
Mo was incorporated in the pores of NaY zeolite by chemical vapor deposition (CVD) using Mo(CO)<sub>6</sub>. The precursors were sulfided in H<sub>2</sub>S/H<sub>2</sub> at 400 °C to form Mo<sub>x</sub>S<sub>y</sub> species within the zeolite framework. To form cluster catalysts with different nuclearity, the catalysts were treated in H<sub>2</sub> at 400 °C after sulfidation. *In situ* X-ray absorption and emission spectroscopy (XAS/XES) was measured using a quartz capillary micro-reactor. Density functional calculations (DFT) were performed using the ORCA quantum chemistry package. Catalytic reactions were carried out in a lab-scale plug flow reactor. Ethene hydrogenation was performed at 200 °C at ambient pressure with a H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> volumetric ratio of 20/1.

## Results and Discussion

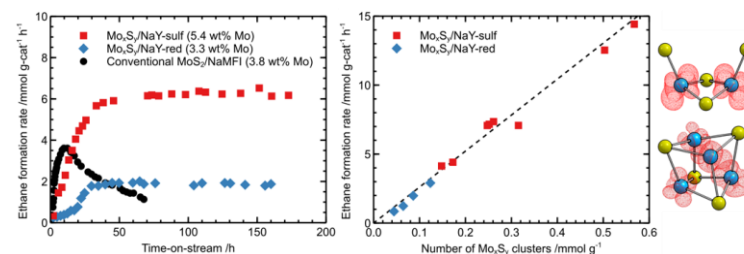
Using CVD followed by thermal treatment in reactive gases, we were able to encapsulate Mo<sub>x</sub>S<sub>y</sub> clusters within the pores of NaY zeolite. Based on EXAFS and S/Mo ratios (determined by elemental analysis) we propose Mo<sub>2</sub>S<sub>4</sub> (sulfided state) and Mo<sub>4</sub>S<sub>4</sub> clusters (reduced state) as the almost exclusively present structures inside the zeolite framework (Table 1). Remarkably, the thermodynamically most stable, lowest energy structures of both clusters obtained from DFT contain unpaired electrons located at the Mo centers (red spheres in illustration Table 1). Investigating catalytic hydrogenation on a traditional catalyst (MoS<sub>2</sub>/NaMFI) and cluster catalysts, we observed two remarkable differences.

**Table 1.** EXAFS fitting parameters of Mo<sub>x</sub>S<sub>y</sub>/NaY-sulf/red and structural parameters of the nitrogenase FeMo-cofactor as a reference (determined by XRD). DFT-optimized lowest energy structures for the two clusters are illustrated on the left.

Catalyst	Path	CN	d / Å
Mo <sub>x</sub> S <sub>y</sub> /NaY-sulf	Mo-S	3.9	2.42
	Mo-Mo	1.3	2.77
Mo <sub>x</sub> S <sub>y</sub> /NaY-red	Mo-S	2.6	2.47
	Mo-Mo	3.3	2.66
Nitrogenase	Mo-S	3	2.34 (from ref. [3])
FeMo-cofactor	Mo-Fe	3	2.70 (from ref. [3])



First, the latter show significantly superior stability without H<sub>2</sub>S added to the feed (Figure 1, left) and secondly, hydrogen is activated in a decidedly different mechanism. In contrast to formation of protic SH-groups like on MoS<sub>2</sub>, molecular clusters stabilize hydrogen as hydride species on the cluster's Mo centers (Figure 1, right). This finding is jointly demonstrated by IR spectroscopy of adsorbed probe molecules as well as DFT. Both, the presence of unpaired electrons (corroborated by EPR spectroscopy) and the activation of hydrogen in form of hydride species add to the list of similarities between TMS clusters existing in zeolites on the one hand and enzymes on the other hand.



**Figure 1.** Ethene hydrogenation rates for different TMS catalysts (from ref. [5]) and DFT-optimized structures of hydrogen adsorbed on bi- and tetranuclear Mo<sub>x</sub>S<sub>y</sub> clusters.

## Significance

TMS are a large group of catalysts in the refining of crude oil and are gaining major importance as replacement for noble metals in electrocatalysis. Improving these systems (e.g., by using the sulfide centers of enzymes) may be a key towards the resource-saving production of energy carriers. Our findings on structure and reactivity of molecular TMS catalysts open an intriguing path towards linking traditional heterogeneous with enzymatic catalysis.

## References

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