Zeolite-Stabilized Di- and Tetranuclear Molybdenum Sulfide Clusters Form Stable Catalytic Hydrogenation Sites

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Abstract: Supercages of faujasite (FAU)-type zeolites serve as a robust scaffold for stabilizing dinuclear (MoSx) and tetranuclear (MoSx) molybdenum sulfide clusters. The FAU-encaged MoS4 clusters have a distorted cubane structure similar to the FeMo-cofactor in nitrogenase. Both clusters possess unpaired electrons on Mo atoms. Additionally, they show identical catalytic activity per sulfide cluster. Their catalytic activity is stable (>150 h) for ethene hydrogenation, while layered MoSx structures deactivate significantly under the same reaction conditions.

Sulfide-based enzymes and the success of transition metal sulfide (TMS) catalysts for hydrotreating reactions have spurred wide interests to understand their activity and selectivity and especially the impact of the cluster size and structure for reductive catalysis. For the nitrogenase family, TMS have recently drawn major interest as cathode materials in electrocatalysis. Despite their similar chemical compositions, the TMS clusters in enzymes are well-defined entities, whereas TMS phases in industrial catalysts have been equally well investigated compared to those in enzyme-based catalysts. In addition to the use of the former as hydrogenation and hydro-defunctionalization catalysts for hydrotreating of refinery fractions and renewable feedstocks, TMS have recently drawn major interest as cathode materials in electrocatalysis. A one-step synthesis could, in contrast, enable the use of such entities as potentially robust highly efficient catalysts. In this context, zeolites represent a promising group of porous supports that provide a stable and well-defined steric environment for the TMS clusters, mimicking partly the pockets of enzymes that host the active center.

Among the methods reported for immobilizing Mo and NiMo sulfide clusters on/in zeolites, ion exchange proves useful yet requires intricate synthesis of the cationic clusters. A one-step synthesis could, in contrast, enable the use of such entities as potentially robust highly efficient catalysts. In this context, zeolites represent a promising group of porous supports that provide a stable and well-defined steric environment for the TMS clusters, mimicking partly the pockets of enzymes that host the active center.

Using leads from Okamoto et al., we used chemical vapor deposition (CVD) and subsequent thermal treatments in reactive gases to incorporate homotopic size- and structure-selective MoSx clusters into the pores of zeolite NaY. The (uniformity of the) geometric structure and the spin state of the MoSx clusters were acquired in the present study by combining X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy (XES), electron paramagnetic resonance (EPR) spectroscopy, and density functional theory (DFT) calculations. A close similarity was revealed between the tetranuclear MoS4 cluster and the Mo site in nitrogenase enzymes. These NaY-encaged MoSx clusters displayed outstanding stability for ethene hydrogenation, much superior to that of a traditional slab-MoS2 catalyst.

Mo(CO)6 encapsulated in a NaY zeolite was treated in H2S/H2 at 673 K for 2 h to form MoSx species within the zeolite (MoSx/NaY-sulf). The zeolite used was almost free of extra-framework Al (EFAl) and remained so after loading Mo and sulfidation (Figure S1). This catalyst was subsequently reduced in pure H2 (MoSx/NaY-red) at 673 K for 2 h. Figure 1 shows the k-weighted extended X-ray absorption spectrum of the MoSx/NaY-red. The k-weighted EXAFS spectrum was obtained by Fourier transforming the Mo K-edge EXAFS data, and the amplitudes were then multiplied by k². The MoSx/NaY-red catalyst displayed a distinct Mo-S, Mo-Mo, and Mo-S-Mo coordination environment, which is consistent with the tetranuclear MoS4 cluster observed in nitrogenase.
fine structure (EXAFS) and Fourier-transformed (FT) EXAFS of these catalysts at Mo K-edge. The corresponding fitted parameters are reported in Table 1. For MoS\textsubscript{x}/NaY-sulf, the Mo-S and Mo-Mo coordination numbers (CN) and interatomic distances (d) together with the S/Mo ratio of ≈2 (determined by elemental analysis) point to the overall cluster composition of Mo\textsubscript{S}. We hypothesize that in this structure, each Mo atom is coordinated to two bridging S atoms and one terminal S atom (either in cis or in trans configuration), resulting in theoretical CN\textsubscript{Mo-Mo} ≈ 1 and CN\textsubscript{Mo-S} ≈ 3. Slightly higher measured coordination numbers (CN\textsubscript{Mo-Mo} ≈ 3.9; CN\textsubscript{Mo-S} ≈ 1.3) are attributed to a minor presence of higher nuclearity species (e.g., a few Mo\textsubscript{2} slabs on the external surface of the zeolite). For Mo\textsubscript{S}/NaY-red, the observed CN\textsubscript{Mo-Mo} and CN\textsubscript{Mo-S} together with the S/Mo ratio of ≈1 suggest the reduced state to be a Mo\textsubscript{S} cluster. Additionally, based on similar values of d\textsubscript{Mo-Mo} and d\textsubscript{Mo-S} we hypothesis the Mo\textsubscript{S} cluster to resemble a distorted Mo\textsubscript{4}-tetrahedron with an S atom sitting on each face. The composition and structure of this reduced state is different from a previously proposed Mo\textsubscript{S} cluster with a cubane-like structure.[9] Instead, we propose that the deduced structure has a close similarity with the MoFe\textsubscript{3}C subunit of the nitrogenase FeMo-cofactor (Table 1). The Mo\textsubscript{S}/NaY-red catalyst was resulfided in H\textsubscript{2}S/H\textsubscript{2} at 673 K for 2 h to form Mo\textsubscript{S}/NaY-resulf. The observed Mo-Mo and Mo-S CN and interatomic distances in Mo\textsubscript{S}/NaY-red were similar to those in Mo\textsubscript{S}/NaY-sulf, suggesting that the transformation between the sulfided and reduced structures is reversible by switching between pure H\textsubscript{2} and H\textsubscript{2}S/H\textsubscript{2} (Figure 3).[9]

Energy dispersive X-ray spectroscopy (EDS) mapping shows an even distribution of Mo across the zeolite particles (Figure S2), proving that Mo and S are not enriched at the outer surface of the crystallites. This indicates that Mo is initially evenly distributed and remains locally anchored as sulfide clusters with two different nuclearities. The decrease in zeolite micropore volume with increasing Mo loading also supports this conclusion (Figure S3). The absence of any larger particles in the high-angle-annular dark field-transmission electron microscopy (HAADF-TEM; Figure S2) showed further that the di- and tetranuclear clusters are the predominant, if not the only, form of Mo\textsubscript{S}, X-ray diffraction patterns of the Mo\textsubscript{S}-containing samples and the parent NaY zeolite show a change in the relative intensities of several diffraction peaks (Figure S4), attributed to a redistribution of Na\textsuperscript{+} cations within the zeolite.[10] This indicates a slight preference of the location of the TMS clusters, requiring, however, additional analysis.

The hypothesized structures of Mo\textsubscript{S} and Mo\textsubscript{S} clusters were optimized using DFT and the results were compared against the experimental data (EXAFS). Interestingly, variations in the number of unpaired electrons in the Mo d-orbitals correlated with the Mo–Mo bond distances, while the Mo-S interatomic distances were insensitive to these changes (Figure 2).

The DFT-computed d\textsubscript{Mo-Mo} (Table S3) obtained for the thermodynamically most stable configurations (spin-multiplicity of 3 for Mo\textsubscript{S} and 5 for Mo\textsubscript{S} match excellently with the values obtained from EXAFS (Table 1). The computed $\Delta E$ however appear to be significantly lower than those observed experimentally, which we attribute to the fact that geometry optimization was performed in gas phase, while for

| Path                  | CN   | d (Å)   | $E_0$ [eV] | $\Delta E$ [eV] | $\sigma^2 \times 1000$ [Å\textsuperscript{2}] | R-factor |
|-----------------------|------|---------|------------|----------------|---------------------------------------------|----------|
| Mo\textsubscript{S}/NaY-sulf | Mo–S | 3.9 ± 0.8 | 2.42 ± 0.01 | 19997         | 0.1 ± 2.4                                  | 6.6 ± 1.5 | 0.027 |
|                       | Mo–Mo | 1.3 ± 1.1 | 2.77 ± 0.03 |               |                                             | 10.3 ± 8.6 |          |
| Mo\textsubscript{S}/NaY-red | Mo–S | 2.6 ± 1.0 | 2.47 ± 0.05 | 19995         | 0.4 ± 5.0                                  | 5.5 ± 5.0 | 0.039 |
|                       | Mo–Mo | 3.3 ± 2.0 | 2.66 ± 0.03 |               |                                             | 6.3 ± 2.6 |          |
| Mo\textsubscript{S}/NaY-resulf | Mo–S | 4.1 ± 0.7 | 2.42 ± 0.01 | 19997         | 0.2 ± 2.1                                  | 6.4 ± 1.3 | 0.023 |
|                       | Mo–Mo | 1.0 ± 1.1 | 2.76 ± 0.03 |               |                                             | 8.2 ± 6.7 |          |
| Nitrogenase           | Mo–S | 3\textsuperscript{[h]} | 2.34\textsuperscript{[h]}, 2.32\textsuperscript{[h]} | 19997         | 0.2 ± 2.1                                  | 8.2 ± 6.7 |          |
| FeMo-cofactor         | Mo–Fe | 3\textsuperscript{[h]} | 2.70\textsuperscript{[h]}, 2.61\textsuperscript{[h]} |               |                                             |          |        |

[a] Data from ref. [1g]. [b] Data from ref. [1f].
the zeolite-encaged clusters, the terminal S atoms are likely to interact with sodium cations in the zeolite, which is expected to elongate the bonds. As these interactions could also lead to charge transfer to/from clusters, we investigated the influence of positive/negative charge on the optimized geometries (Figure S5). The calculations indicate that the structural parameters of these clusters are influenced more by the spin-multiplicity than by the net charge on the clusters. Based on computed Gibbs free energies (Figure 2 and Tables S1 and S2), the lowest-energy structures have a spin-multiplicity of 3 (two unpaired electrons) and 5 (four unpaired electrons) for Mo$_2$S$_4$ and Mo$_4$S$_4$ (Figure 3), respectively. For Mo$_2$S$_4$, the cis configuration was found to be more stable and is further examined.

As DFT calculations correspond to one unpaired electron per Mo for both clusters, the presence of unpaired electrons on Mo was also deduced from the EPR measurements (Figure 4 left). The EPR spectra show an intense central line with g-values close to 2, in close agreement with the g-values reported for unpaired electrons in Mo species of different formal oxidation states in nitrogenase, nitrate reductase, and sulfur-bridged Mo dimer clusters. Although EPR signals with $g \approx 2$ are commonly assigned to $S = \frac{1}{2}$ systems, these signals may also be interpreted as $M_s \pm 1$ transitions of systems with higher spin-multiplicities, e.g., cis-Mo$_2$S$_4$ (spin-multiplicity = 3) and Mo$_4$S$_4$ (spin-multiplicity = 5), with a large zero field splitting. Due to the lack of spin quantification, an in-depth electronic spin analysis of Mo$_x$S$_y$ clusters proposed in this work is presently not achievable. It must also be noted that a mixture of clusters with different spin-multiplicities may be present as the DFT-computed Gibbs free energy difference between systems with slightly different multiplicities is relatively small (Figure 2 and Table S1).

The DFT calculations unambiguously support our finding that the unpaired electrons are indeed located on the Mo atoms of both Mo$_x$S$_y$ clusters (Figure 4, right and Figure S6). In this regard, it is important to note that ionic clusters would result in formal Mo oxidation states of +4/+2 (assuming neutral Mo$_2$S$_4$/Mo$_4$S$_4$ clusters) which could not possess single unpaired electrons due to their even number of total valence electrons. However, the Mo--S bonds in these nanoclusters are likely to be covalent in character, which is supported by Hirshfeld/Mulliken population analysis and Mayer bond orders computed using DFT (Tables S4 and S5).

Further confirmation of the hypothesized structures of NaY encapsulated Mo$_x$S$_y$ clusters was deduced from Mo Kα high energy resolution fluorescence detected X-ray absorption near edge structure (HERFD-XANES) and Mo Kβ valence-to-core (VtC) XES. The VtC XES spectra of Mo$_x$S$_y$/NaY-sulf/red catalysts are in close agreement with the simulated spectra of the optimized Mo$_x$S$_y$ clusters and Mo$_x$S$_y$ structures (Figure S7 and Table S6) validating the structures suggested in this work. In addition, HERFD-XANES shows a shift towards lower absorption energies for the reduced catalyst supporting the proposed reduction of Mo centers in a pure H$_2$ atmosphere (Figure S10).
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Interestingly, when subjecting the two clusters catalysts to a stream of ethene and H₂, no activity was observed at the very beginning, but both catalysts gained activity and reached a steady-state over a time span of ~30 h (Figure 5). Elemental analysis of the spent MoSₓ/NaY-sulf sample showed a loss of sulfur that corresponded to approximately one S per cluster. Thus, we hypothesize that partial sulfur loss from the fully sulfided MoSₓ cluster may account for the generation of true active sites (S-vacancies) while the original clusters are inactive. Given the high reduction temperature (673 K in pure H₂), further reduction and sulfur loss is rather unlikely for the MoSₓ/NaY-red sample at the reaction temperature of 473 K and the induction period could be caused by restructuring.

While it would also be very important to understand a potential response of the Mo spin states to its local coordination environment, this is to be further investigated by in situ spectroscopy (EPR and XAS in particular) that monitors the dynamic evolution of the structure and chemical compositions of the active sites at reaction conditions.

For MoSₓ/NaY-sulf/red catalysts, a linear increase of the steady-state ethane formation rate (per gram of catalyst) was observed with an increasing loading of clusters (Figure 5). The parent NaY zeolite itself (no EFAl species or Brønsted acid sites; Figures S1 and S11) did not exhibit hydrogenation activity. Therefore, we conclude that the measured activity stems solely from MoSₓ clusters that are homogeneous in nature. Surprisingly, the linear rate increase was identical for di- and tetramers indicating that each cluster forms the same number of equally active sites.

The cluster catalysts showed stable steady-state conversion rates (for at least 7 days), allowing to conclude that the active sulfide sites hosted in the zeolite cages remained stable, in contrast to previous studies that either lacked evaluation of the stability metric or clearly noted deactivation/degradation of the active structures. A traditional MoSₓ/NaMFI catalyst that featured extended slabs, however, deactivated markedly after reaching the maximum activity (Figure 5). The NaMFI zeolite used as a support is free of Brønsted acid sites and did not show any activity under the probed conditions. We, therefore, conclude that deactivation results from degradation of the MoS₂ phase without supply of sulfur in the reactant stream.

In summary, we have shown that di- and tetrameric MoSₓ clusters can be stabilized in a homogeneous form by zeolite Na-FAU. The active clusters are homogeneously distributed in the zeolite and are essentially homotopic. The specific catalytic activity of these clusters for ethene hydrogenation is identical. The tetrameric cluster is structurally similar to the Mo site of the FeMo-cofactor in nitrogenase. DFT-based optimization of the cluster geometry and free energy calculations predict that both clusters contain a single unpaired electron at each Mo atom. While the intrinsic catalytic activity is similar to those of a conventional supported MoS₂ catalyst, the latter deactivates markedly during time on stream while both the di- and tetrameric MoSₓ cluster-based catalysts are stable for days of operation. Thus, the zeolite-supported MoSₓ cluster catalysts are a promising new class of robust, bio-inspired hydrogenation catalysts that create exciting opportunities with respect to chemical and structural variability for catalysis.

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Conflict of interest

The authors declare no conflict of interest.

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