Zeolite-encapsulated molybdenum sulfide clusters activate and stabilize hydrogen in the form of hydride species

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Introduction

Transition metal sulfides (TMS) are a prominent class of heterogeneous catalysts with a wide range of applications including hydrotreating of petroleum-derived feedstock, upgrading of bio-derived feedstock, water-gas shift reaction, and more recently, as alternatives to precious metals in electrocatalytic applications. These TMS catalysts are typically composed of sulfides of Mo and/or W (promoted with Ni/Co). While the link between these catalysts and enzymes-based metal-sulfur (M-S) active sites seems intuitive, a clear link has not been substantiated so far.

Zeolites are ideal supports for forming well-defined TMS clusters due to their stable and three-dimensional porous framework. Therefore, using nature as a role model, we have synthesized well-defined dimeric (Mo_2S_4) and tetrameric (Mo_4S_4) molybdenum sulfide clusters encapsulated within the micropores of NaY zeolite.[1] We have investigated in detail the electronic and structural properties of these pore-confined clusters using X-ray absorption and emission spectroscopy (XAS/XES) and density functional theory (DFT) calculations. We show that these clusters are structurally and electronically similar to the nitrogenase enzyme's FeMo-cofactor and activate hydrogen in the the form of homolytically disscoaited hydride species stabilized on Mo centers. Interestingly, these clusters show remarkable stability for ethene hydrogenation. We discuss in detail how these clusters activate hydrogen and how their structures adapt to the reaction environment, a central fundamental question that has remained unaddressed so far for these systems.

Results and Discussion

Extended X-ray absorption fine structure (EXAFS) of Mo_2S_4/NaY and Mo_4S_4/NaY catalysts was used to determine Mo-S and Mo-Mo coordination numbers (CN) and interatomic distances (Figure 1a,b). The CN_{Mo-S} and CN_{Mo-Mo} in the sulfided Mo_2S_4/NaY were estimated to be ~3.9 and ~1.3, respectively. Similarly, in the reduced Mo_4S_4/NaY catalyst, CN_{Mo-S} and CN_{Mo-Mo} were determined to be ~2.6 and ~3.2. Based on CN and interatomic distances determined from EXAFS and S/Mo obtained from

elemental analyses (~2 in Mo_2S_4/NaY and ~1 in Mo_4S_4/NaY), the Mo_xS_y clusters were confirmed to be Mo_2S_4 and Mo_4S_4, respectively. The geometries of the proposed clusters were optimized using DFT and the thermodynamically most stable structures were determined (Figure 1d). DFT calculations supported by EPR spectroscopy measurements predict that these clusters contain unpaired electrons on Mo atoms.

These cluster catalysts exhibited remarkable stability for ethene hydrogenation in the absence of sulfur feed while the classic layered MoS_2 deactivated significantly under the same conditions (Figure 1c). Using IR spectroscopy of adsorbed probe molecules, supported by DFT simulations, we show that these catalysts activate H_2 in a homolytic fashion and stabilize it in the form of hydride species localized on Mo (Figure 1e). In strong contrast to classic MoS_2 catalysts, stabilization of H_2 as sulfhydryl (SH) groups was found to be thermodynamically disfavored; instead, these molecular clusters show distinct similarities to the FeMo-cofactor which has also been shown to partly stabilize H_2 as hydride species.

We envision that these zeolite-supported Mo_xS_y cluster catalysts could be the basis of a promising new class of robust, bio-inspired catalysts that create exciting opportunities with respect to chemical and structural variability. Understanding their unique structural, electronic, and catalytic properties will open exciting avenues for the application of these novel catalysts for a variety of catalytic reactions.
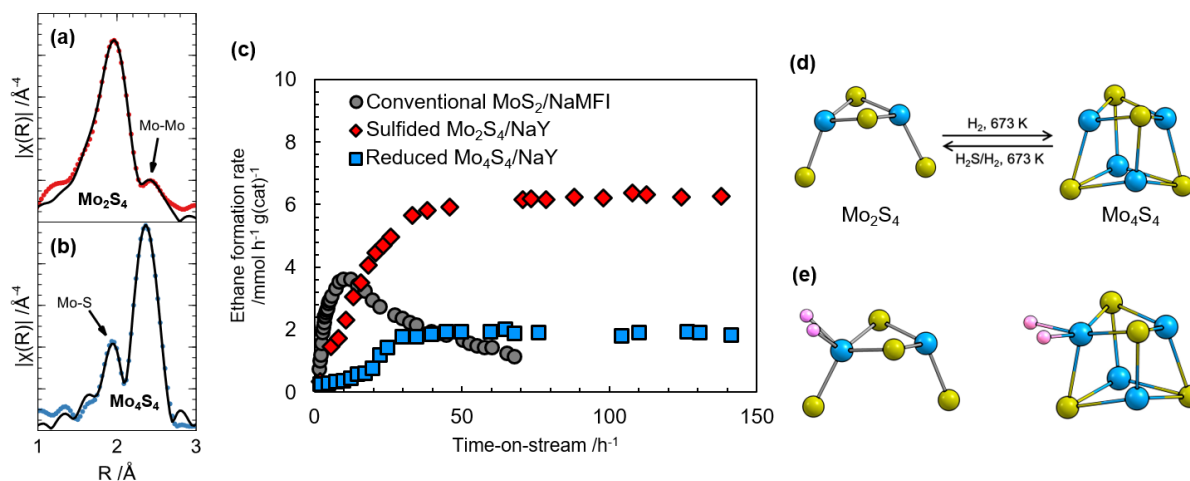

Figure 1. (a,b) Fourier-transformed EXAFS of Mo_2S_4/NaY (red) and Mo_4S_4/NaY (blue) (c) Ethane formation rates as a function of time-on-stream. (d,e) DFT-optimized geometries of bare Mo_2S_4 and Mo_4S_4 clusters and with H_2 molecule dissociatively adsorbed on Mo.

References

1. R. Weindl, R. Khare, L. Kovarik, A. Jentys, K. Reuter, H. Shi, J. A. Lercher, Angewandte Chemie International Edition, 60(17), 9301-9305 (2021).