Zeolite-encapsulated molybdenum sulfide clusters activate and stabilize hydrogen as hydride species

Rachit Khare; Roland Weindl; Andreas Jentys; Johannes A. Lercher

Department of Chemistry and Catalysis Research Center, Technical University of Munich, Lichtenbergstraße 4, 85748 Garching, Germany

Introduction

Transition metal sulfides (TMS) are a prominent class of catalysts with a wide range of applications including hydrotreating of petroleum-derived feedstock, upgrading of bio-derived feedstock, (reverse) 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 and/or Co). While the link between these catalysts and enzyme-based metal-sulfur moieties seems intuitive, a clear link has not been established yet.

Zeolites are ideal supports for encapsulating well-defined TMS clusters due to their stable 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 stabilized within the micropores of NaY (denoted as Mo_2S_4/NaY and Mo_4S_4/NaY, respectively).[1] We have investigated in detail the electronic and structural properties of these pore-confined clusters using X-ray absorption spectroscopy and density functional theory (DFT) calculations. We show that these clusters are structurally and electronically similar to the nitrogenase enzyme's FeMo-cofactor. Interestingly, these clusters show remarkable stability for ethene hydrogenation. We also show, utilizing infrared (IR) spectroscopy of adsorbed probe molecules supplemented with additional DFT calculations, that these clusters activate H_2 in the form of homolytically-dissociated hydride species stabilized on Mo centers. 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

The Mo-S and Mo-Mo coordination numbers (CN) in the Mo_2S_4/NaY catalyst were estimated, from extended X-ray absorption fine structure (EXAFS) measurements, to be ~3.9 and ~1.3, respectively. Similarly, in the Mo_4S_4/NaY catalyst, CN_{Mo-S} and CN_{Mo-Mo} were determined to be ~2.6 and ~3.2. Based on these CNs 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 favorable structures were obtained (Figure 1d). DFT calculations supported by EPR spectroscopy predict that these clusters contain unpaired electrons on Mo atoms.

These 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 calculations, we show that these catalysts activate H_2 in a homolytic fashion and stabilize it in the form of hydride species localized on Mo atoms (Figure 1e). In strong contrast to classic MoS_2 catalysts, stabilization of hydrogen as sulfhydryl (SH) groups was found to be thermodynamically unfavorable; instead, these molecular clusters show distinct similarities to the nitrogenase enzyme's FeMo-cofactor, which has also been shown to partly stabilize hydrogen 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 applications.
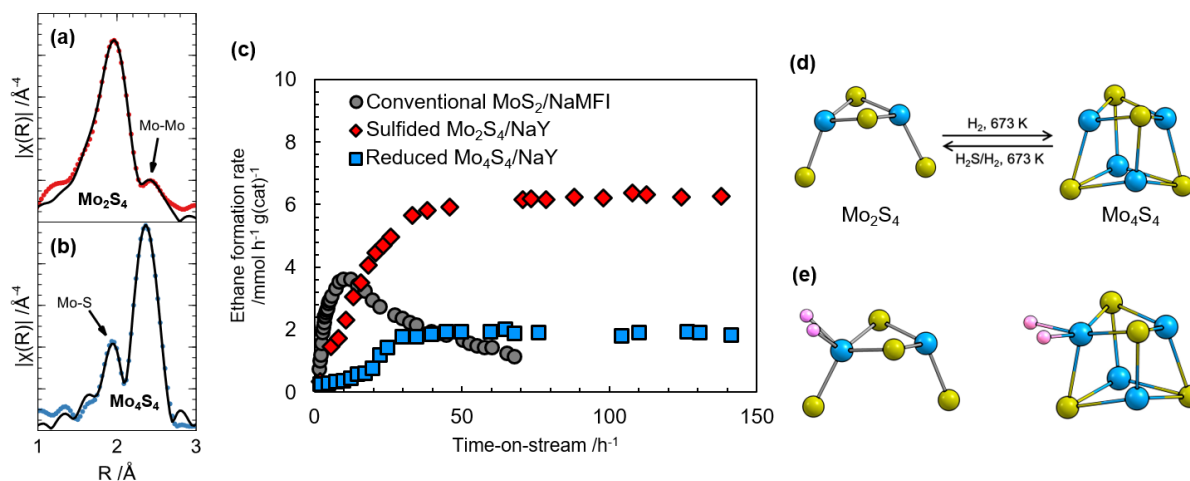
Figure 1. (a,b) Fourier-transformed EXAFS of Mo_2S_4/NaY (red) and Mo_4S_4/NaY (blue) (c) Ethene hydrogenation rates as a function of time-on-stream. (d,e) DFT-optimized geometries of Mo_2S_4 and Mo_4S_4 clusters with/without H_2 dissociatively adsorbed on Mo.

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).