Zeolite stabilized molybdenum sulfide clusters activate hydrogen as hydride species and form stable catalytic hydrogenation sites

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Introduction

Only one single group of enzymes is able to introduce nitrogen into the metabolic cycle by making use of dinitrogen as most abundant source: nitrogenases.[1] Extensive experimental and computational studies have revealed that three different transition metal sulfide (TMS) clusters play a crucial role in enzymatic N_2 fixation: a Fe_4S_4 tetramer, the P-cluster (Fe_8S_7), and a third cluster Fe_7MS_9C (M: Fe, Mo, V) of which the Mo form (FeMo-cofactor) is the most extensively studied one.[2] Long before the composition or the structure of the active sites in nitrogenase enzymes were known, industry developed and implemented TMS as heterogeneous catalysts primarily for hydrotreating applications. These catalysts, typically composed of sulfides of Mo and/or W (promoted with Ni and/or Co), are used either unsupported or supported on oxidic supports.[3] Despite their chemical compositions being similar, the enzyme's active TMS phase comprises of small well-defined clusters, whereas the TMS phase in industrial catalysts is present in the form of bigger slab-like structures that depict two-dimensional bulk sulfide phase.

Zeolites are ideal supports for forming well-defined TMS clusters due to their stable and well-defined porous framework. Therefore, using nature as role model, we have synthesized small well-defined dimeric and tetrameric Mo_xS_y clusters encapsulated within the micropores of NaY zeolite. We have investigated in detail the electronic and structural properties of these pore-confined clusters using X-ray absorption spectroscopy measurements and density functional theory (DFT) calculations. We show that these clusters are structurally and electronically similar to the FeMo-cofactor of the nitrogenase enzyme. Interestingly, these clusters show remarkable stability for ethene hydrogenation reaction. We also discuss how these clusters activate hydrogen and how their structures dynamically adapt to the reaction environment, a central fundamental question that has remained unaddressed so far for these systems.

Materials and Methods

NaY-encapsulated molybdenum sulfide precursors were prepared via chemical vapor deposition (CVD) of molybdenum hexacarbonyl.[4] $Mo(CO)_6$ containing NaY zeolites (Si/Al ~2.5) were sulfided in H_2S/H_2 mixture at 673 K to form sulfided Mo_xS_y/NaY catalysts (denoted as Mo_xS_y/NaY-sulf). The Mo_xS_y/NaY-sulf catalyst was then reduced in H_2 at 673 K to form the reduced Mo_xS_y/NaY catalyst (denoted as Mo_xS_y/NaY-red). The structure of NaY-encapsulated Mo_xS_y phase in these materials was investigated using X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES), performed at the European Synchrotron Radiation Facility (ESRF) and the German electron synchrotron (DESY). Experimental results were supported by detailed DFT calculations performed using ORCA quantum chemistry package. Infrared spectroscopy of adsorbed probe molecules was utilized to investigate adsorption and activation of hydrogen in these cluster catalysts. Spectroscopic and computational studies were complemented with additional characterization including XRD, EPR spectroscopy, ^{27}Al-MAS-NMR spectroscopy, elemental analysis, HAADF-TEM, EDX, and N_2 sorption measurements. The synthesized catalysts were tested for ethene hydrogenation reaction. Ethene hydrogenation was performed at 473 K and ambient pressure with a typical H_2/C_2H_4 volumetric ratio of 20:1. Product composition was analyzed by online gas chromatography.

Results and Discussion

Figure 1a shows the extended X-ray absorption fine structure (EXAFS) of sulfided and reduced Mo_xS_y/NaY catalysts. Mo-S and Mo-Mo coordination numbers (CN) in Mo_xS_y/Na-sulf were determined to be ~3.9 and ~1.3, respectively. Similarly, in the reduced Mo_xS_y/NaY-red catalyst, CN_{Mo-S} and CN_{Mo-Mo} were determined to be ~2.6 and ~3.2. Based on EXAFS and S/Mo ratios obtained from elemental analysis (~2 in Mo_xS_y/NaY-sulf and ~1 in Mo_xS_y/NaY-red), the Mo_xS_y clusters were identified to be Mo_2S_4 and Mo_4S_4. The structures clusters were optimized using DFT and thermodynamically most stable structures were determined (Figure 1b). Interestingly, the tetrameric Mo_4S_4 cluster was found to be structurally and electronically similar to the FeMo-cofactor in the nitrogenase enzyme. DFT calculations supported by EPR spectroscopy measurements also predicted that both dimetric and tetrameric clusters contain a single unpaired electron at each Mo site.

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. We show that these catalysts activate H_2 in a homolytic fashion and stabilize it in the form of hydride species on their Mo centers (Figure 1c). In strong contrast to classic slab-like bulk 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. The adsorption of H_2 on the Mo centers was verified by DFT calculations and Fourier-transform infrared spectroscopy of adsorbed probe molecules.
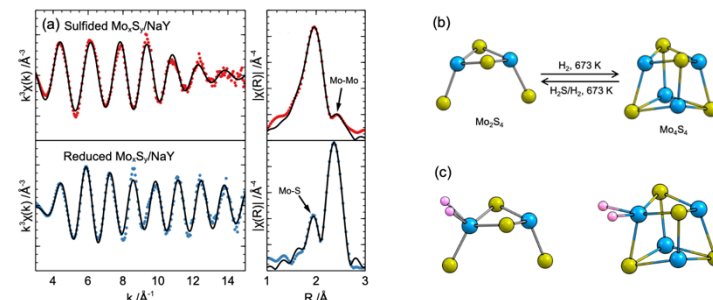
Figure 1. (a) EXAFS of Mo_xS_y/NaY-sulf and Mo_xS_y/NaY-red catalysts. **(b)** Proposed structures of Mo_2S_4 and Mo_4S_4 clusters. **(c)** DFT-optimized geometries of Mo_2S_4 and Mo_4S_4 clusters with one dissociatively adsorbed H_2 molecule on a Mo atom.

Significance

Zeolite-supported Mo_xS_y clusters are a promising new class of robust, bio-inspired hydrogenation catalysts that create exciting opportunities with respect to chemical and structural variability for catalysis. Understanding their unique structural, electronic, and catalytic properties will open exciting avenues for the application of these novel catalysts for a variety of heterogeneous catalytic reactions.

References
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