

SONOCHEMICALLY GENERATED MoS₂-BASED CATALYSTS

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Sonochemistry arises from acoustic cavitation: Gas bubbles in a liquid irradiated with sound of sufficient intensity can grow to a resonance size and undergo an implosive collapse. This is a near-adiabatic process in its latest stages. The temperature of the localized hot spots thus generated approach 5000 K with pressure of at least 400 atm and lifetimes of <100 nsec, which gives cooling rates on the order of 10^{10} K/s.^{1,2} The energy of the collapsing bubble can be used to decompose volatile inorganic and organometallic species, which is the basis of sonochemical synthesis of nanophasic materials discussed below.³

Sonochemically Generated HDS Catalyst

Co, Ni and Co-Ni promoted/supported MoS₂ catalysts have been synthesized by sonochemical decomposition of metal carbonyls in presence of sulfur (and support, if applicable) in isodurene, similar to previously reported synthesis of sonochemically generated MoS₂.⁴ Co-Mo-S/Al₂O₃ was prepared by sonication of Mo(CO)₆ and Co₂(CO)₈ in presence of sulfur and Al₂O₃ in isodurene. Ni-Mo-S/Al₂O₃ was prepared by the deposition of Ni on Al₂O₃ by incipient soaking in an aqueous solution of Ni(N₂H₃COO)₃N₂H₅ followed by reduction at 400 °C under He/H₂. The resulting Ni/Al₂O₃ was then sonicated in presence of Mo(CO)₆ and sulfur. Doubly promoted (Co and Ni) catalyst was generated by combining both methods.⁵

Activity and the long-term stability of these catalysts were studied for HDS of thiophene and dibenzothiophene (DBT). HDS activity measurements for DBT were accomplished using a home-built high-pressure vessel with a sample withdrawal system, and products were analyzed using GC-MS. Activity measurements (Figure 1) and product distribution (Figure 2) were determined at high [DBT] where the kinetics were zero order. As can be seen, sonochemical catalysts have significantly higher activities for HDS of DBT, with identical selectivity towards biphenyl. Similar trends in activity were observed for the HDS of thiophene in a flow microreactor, with sonochemical catalysts displaying comparable or better stability over the course of 5 days.

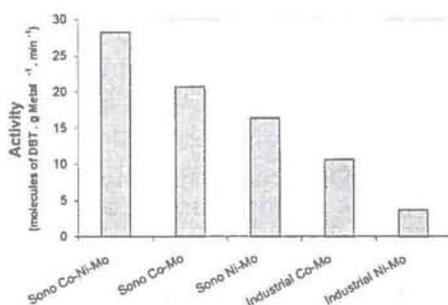


Figure 1. Activity of supported catalysts for HDS of DBT per gram.

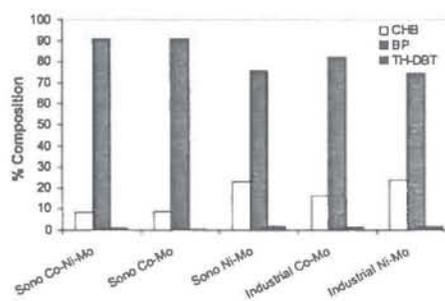


Figure 2. Relative selectivity of the evaluated HDS catalysts.

CHB = cyclohexylbenzene, BP = biphenyl; TH-DBT = tetrahydroDBT

Scanning electron micrographs showed individual catalyst particles sitting on top of the surface of Al_2O_3 (Figure 3). TEM showed particles with highly disordered MoS_2 lattice fringes with many breaks and discontinuities (Figure 4). In contrast, ordered stacking of MoS_2 layers were observed in conventional catalysts. XPS analysis showed a three to fivefold surface enhancement of Mo for sonochemical catalysts, but no surface enhancement for the commercial counterparts. These findings serve to explain the higher activity of the sonochemical catalysts.

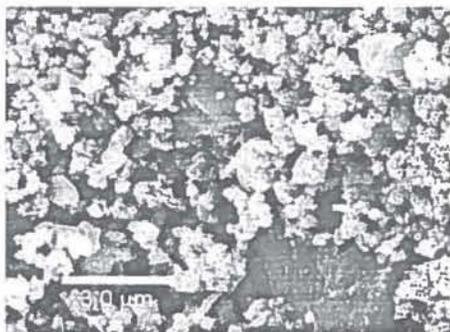


Figure 3. SEM of sonochemical Co-Mo-S/ Al_2O_3 showing individual catalyst clusters decorating Al_2O_3 surface.

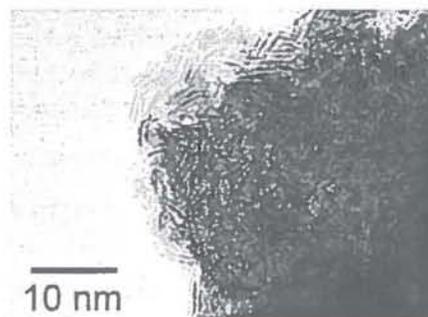


Figure 4. TEM of sonochemical Co-Mo-S/ Al_2O_3 showing highly disordered MoS_2 layer.

The Local Environment of Co in Co-Mo-S Catalysts

In 1981, Topsøe and co-workers, using ^{57}Co Mössbauer Emission Spectroscopy, conclusively demonstrated that Co in promoted MoS_2 catalyst is in a unique environment (dubbed the “CoMoS” phase), and that there is a direct correlation between the signal contributed by this Co phase and the HDS activity of the catalyst.⁶ Since then, great effort has been made to ascertain the structure of this “CoMoS” phase.⁷⁻⁹

We have employed XAS in order to study the local environment of Co in commercial and sonochemical Co-Mo-S/ Al_2O_3 catalysts. Mo K-edge data suggests that in both samples, Mo is predominately present as MoS_2 . Mo-Co interactions were not observed, which suggests that Co is predominately on the surface of the catalyst (decorating the edges of the MoS_2 slabs). Analysis of the Co K-edge data for the industrial catalyst suggests that Co neighbors 1-2 Mo atoms at a distance of 2.89 Å and is coordinated to 4-5 sulfur atoms at a distance of 2.26 Å. The sonochemical catalyst is similar, with Co-S coordination of 5.0 ± 0.8 at a distance of 2.24 Å. The Co-Mo coordination could not be discerned unambiguously for the sonochemical catalysts. Possibility of Co-Co interactions was explored, but addition of a Co neighbor did not improve the fit sufficiently and therefore its presence is ambiguous. The $1s \rightarrow 3d$ transition peak (intense for non-centrosymmetrically coordinated environments metals) is intense for Co_9S_8 where 8 out of 9 sulfurs are tetrahedrally coordinated, but less intense for industrial and sonochemical catalysts. This suggests that the Co in these catalysts is in a pseudo-centrosymmetric environment.

Based on the coordination number, bond length and XANES data, we believe that Co has a distorted square planar or tetrahedral structure, which becomes square

pyramidal upon the coordination of a substrate (such as DBT). Three non-minimized structures are shown below (Figure 5). It should be noted that considering the anisotropy of MoS₂ and the fact that it is supported on alumina, the proposed structural models are speculations. Figure 5A shows a structure that is based on work by Prins *et al*, with a pseudo-square planar Co neighboring two Mo atoms.⁹ Figure 5B shows a possible structure with Co neighboring one Mo atom in a distorted tetrahedral geometry, which can become square pyramidal upon coordination of a substrate. Figure 5C shows a structure with two neighboring Co atoms in a square planar/square pyramidal geometry.

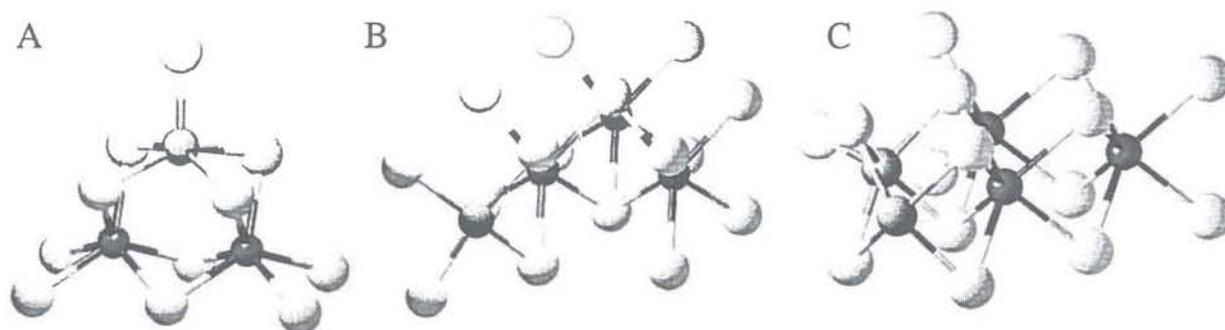


Figure 5. CoMoS models proposed based on XAS data.

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