

Cluster approach to synthesis of ternary metal sulfides: using molybdenum disulfide single-layers as a precursor

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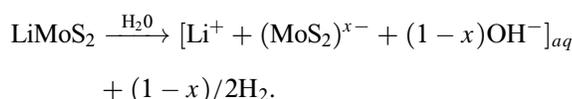
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The reactivity of negatively charged $(\text{MoS}_2)^{x-}$ layers in aqueous single-layer dispersions resembles that of molecular Mo-S cluster compounds. These layers form covalent bonds with metal (M) cations ($M = \text{Cu}, \text{Ag}, \text{Pb}, \text{Cd}, \text{Hg}, \text{Pd}$) giving rise to ternary metal sulfides $M_z\text{MoS}_2$ whose Mo network contains direct Mo-Mo bonds.

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Lithiation of MoS_2 is known to result in solid ionic compound $\text{Li}^+(\text{MoS}_2)^-$ containing negatively charged $(\text{MoS}_2)^-$ layers [1]. These layers can be considered as extended quasi-bidimensional anionic $[\text{S}-\text{Mo}-\text{S}]^{n-}$ clusters whose electronic and chemical nature (valence electron concentration per Mo atom and presence of outer-shell sulfur atoms) allow to expect a behaviour resembling that of molecular Mo-S clusters (Mo_6S_8 , for instance). The main structural feature of the latter, caused by their electronic structure, is the existence of Mo-Mo bonds in the cluster framework. As to chemical reactivity, their sulfur ligands easily coordinate with extra-metal cations [2].

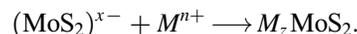
Exfoliation of solid LiMoS_2 in aqueous medium was already shown to produce a dispersed system containing negatively charged $(\text{MoS}_2)^{x-}$ extended cluster species separated by water molecules, with their sulfur atoms accessible for coordination [3,4]:



The approach presented here consists in the use of these cluster-like species as a precursors in chemical reactions.

Results and Discussion

We found recently [5] that re-stacking exfoliated MoS_2 layers in the presence of some M cations yields powdered ternary metal sulfides of the general composition $M_z\text{MoS}_2$ ($M = \text{Cu}, \text{Ag}, \text{Cd}, \text{Pb}, \text{Hg}, \text{Pd}$):



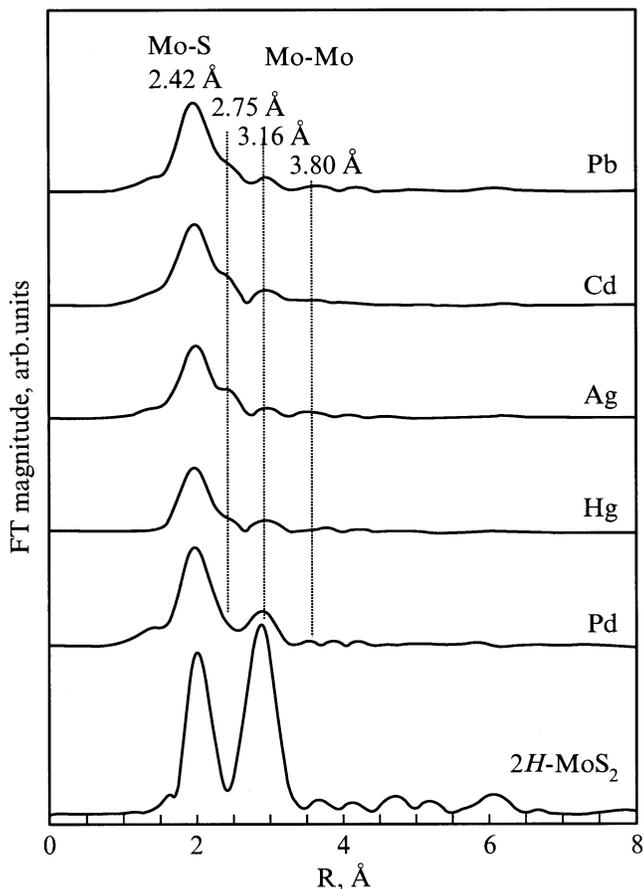
As it follows from EXAFS data obtained at the M K- ($M = \text{Cu}, \text{Ag}, \text{Pd}, \text{Cd}$) and M L_{III}- ($M = \text{Hg}, \text{Pb}$) edges, the closest atomic environment of the M atoms in $M_z\text{MoS}_2$ is composed exclusively of S atoms. This confirms incorporation, between neighboring S-Mo-S sandwiches, of metal cations forming covalent bonds with S atoms of the matrix and agrees with XRD results on the lattice expansions observed for $M_z\text{MoS}_2$ (Table). There are two types of vacant sites in the MoS_2 interlayer space: octahedral and tetrahedral ones. Analysis of the guest metal coordination environment indicates that it is strongly disordered (particularly, for Ag and Hg, see reduced coordination numbers) and that incorporated metal cations tend to approach coordination which are typical for given metal in sulfur surrounding (Table).

Interlayer spacing expansions with respect to parent MoS_2 (Δc) and parameters of closest environment around guest M atoms in $M_z\text{MoS}_2$

$M_z\text{MoS}_2$	$\Delta c, \text{Å}$	N_{M-S}	$R_{M-S}, \text{Å}$	Presumable coordination
$\text{Pb}_{0.18}\text{MoS}_2$	1.0	5.7	2.87	Octahedral
$\text{Cd}_{0.20}\text{MoS}_2$	0.4	4.0	2.55	Tetrahedral
$\text{Cu}_{0.35}\text{MoS}_2$	0.1	3.1	2.29	Tetrahedral
$\text{Ag}_{0.86}\text{MoS}_2^*$	0.8	1.0(+0.5Ag-Ag at 2.87 Å)	2.40	Strongly distorted tetrahedral
$\text{Pd}_{0.45}\text{MoS}_2^{**}$	0.05	1.5(+5.1 Pd-Pd at 2.73 Å)	2.33	Tetrahedral
$\text{Hg}_{0.20}\text{MoS}_2$	0.2	1.1	2.37	Strongly distorted octahedral

* (95% $\text{Ag}_{0.82}\text{MoS}_2$ +5%Ag).

** (60% $\text{Pd}_{0.25}\text{MoS}_2$ +40%Pd).



Fourier transforms of Mo K -edge spectra for $M_z\text{MoS}_2$ and $2H\text{-MoS}_2$.

Formation of the ternary compounds is evidently accompanied by electron transfer from the negatively charged $(\text{MoS}_2)^{x-}$ layers to some metal cations (Ag(I), Pd(II), Hg(II), Cu(II)) involved. This results in reduction of part of these cations in the course of reaction. In the case of Pd, Ag, and Hg, it leads to appearing of additional phases (metallic Pd, Ag, or Hg(I) compounds) along with the phase of ternary sulfide, as it was evidenced by XRD and EXAFS. It is interesting that in the case of Cu(II) taken in reaction, the resulting Cu(I) cations occupy guest positions in the structure of ternary sulfide so that all the intercalated Cu ions are Cu(I), as it follows from XPS data [6].

Despite the decrease of the negative charge on S–Mo–S layers due to redox process, a part of the charge does remain on these layers in ternary compounds, being balanced by covalently bonded guest M cations. It means that part of the electrons transferred to MoS_2 layers on lithiation should be retained on d orbitals of the Mo atoms. This can stabilize the distortions of the Mo network in the compounds obtained. Indeed, EXAFS measurements at Mo K -edge evidenced strong changes of the host structure in the $M_z\text{MoS}_2$ compared to the parent $2H\text{-MoS}_2$. Instead of unique Mo . . . Mo contact at 3.16 Å in the parent MoS_2 , three Mo–Mo distances appear in the ternary compounds

(Figure). The shorter distance (at about 2.75 Å) corresponds to direct Mo–Mo bonds in the layers.

From the present study it appears that $(\text{MoS}_2)^{x-}$ layers in single-layer dispersions are effectively capable to coordinate with metal cations by sulfur atoms and to produce ternary metal sulfides. The host structure of these ternary compounds exhibits strong distortions due to periodic in-layer displacements of the Mo atoms which form direct Mo–Mo bonds.

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