Experimental and theoretical X-ray spectroscopic study of electronic structure of sulfur-contained transition metal complexes

Anastasiya Fedorenko,
Anton Nikolenko, Denis Ivlyushkin, Pavel Zavertkin,
Galina Semushkina, Svetlana Lavrukhina, Yakov Fomenko, Pavel Petrov

NIIC SB RAS
BINP SB RAS
Advanced applications for transition metal sulfides and polysulfides

Growing interest is in compounds containing sulfide and disulfide groups, which may perform as alternative renewable energy sources and environmentally pure catalytic technologies. Among the transition metal sulfides, binuclear and trinuclear clusters deserve special attention. The coordination of terminal ligands of various nature affects the electronic structure of clusters, which could improve functional properties such as nonlinear optical properties, reactivity, and other physicochemical properties.

Disulfides
MoS$_2$

Polysulfides
MoS$_5$

Hybrids/Composites
MoS$_x$/Graphene

Sulfide Clusters
[Mo$_3$S$_{13}$]$^{2-}$

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Model active sites of Mo-S compounds

Binuclear and trinuclear transition metal clusters modified with various terminal ligands have great prospects as catalysts or precursors with higher catalytic activity, and could be considered convenient structural models of active centers of industrial catalysts.

Types of sulfide transition metal clusters

Types of disulfide groups – possible active sites

For example, the catalytic activity of materials based on trinuclear clusters or MoS$_2$ nanoparticles with different morphologies is associated with a large number of disulfide groups in the catalyst structure.
X-ray spectroscopy methods

An important issue in obtaining new functional materials is the characterization of their atomic and electronic structures. X-ray spectroscopy provides information about both the atomic and the electronic structure of the studied compounds.

NEXAFS Near edge X-ray absorption fine structure
SK\(\beta\)- and MoL\(_{2,3}\)-edge NEXAFS spectra were measured in the transmission mode at Cosmos beamline at the VEPP-4M storage ring of BINP SB RAS.
SL\(_{2,3}\)- and MoM\(_{2,3}\)-edge NEXAFS spectra were recorded using the Russian-German beamline (RGBL) at BESSY II (Helmholtz-Zentrum Berlin, Germany).

XPS X-ray photoelectron spectroscopy
XPS measurements were performed in a Phoibos-150 spectrometer (Specs, Germany) using a monochromatic Al K\(\alpha\) source.

XES X-ray emission spectroscopy
SK\(\beta\)- and MoL\(\beta\)\(_{2,15}\)-spectra was measured using x-ray spectrometer “Stearat”. A quartz crystal with the (10-11) plane was used as crystal analyzer. The detector was gas flow proportional counter (90% argon and 10% methane, atmospheric pressure).
On example of such cluster compounds, it can be seen that the S2p binding energy of different types of disulfide ligands can differ by 2 eV. This reflects the degree of covalent interaction of a metal atom with a disulfide ligand. However, when characterizing new functional materials, it should be noted that the position of the S2p line of the most active catalytic centers coincides with other possible sulfur-containing groups and their study requires additional research methods.
S L_{2,3}^{-} and Mo M_{2,3}^{-} edge NEXAFS spectra

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10.2113/gscanmin.43.6.1811
SK- and MoL$_{2,3}$-edge NEXAFS spectra

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Mo L$_{2,3}$-edge XANES

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SK- edge NEXAFS spectra

Calculations details:
ADF
TDDFT
B3LYP*/QZ4P
XES spectra

SKβ spectra

σ-MO (S3p z AO),
π-MO (S3p x, S3p y AO),

π*-MO (S3p x, S3p y AO)

KSCN
S 8
XPS valent band for $S_2^-$ in ZrS 3

Intensity, a.u.
Photon energy, eV

$[\text{Mo}_3\text{S}_7(\text{dtc})\text{Br}]$
$\text{Mo}_3\text{S}_7\text{Br}_4$
$[\text{Mo}_3\text{S}_4\text{tu}_8\text{H}_2\text{O}]\text{Cl}_4$
$(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]$
XES spectra

Experimental and theoretical X-ray emission SKβ spectra for $(NH_4)_2[Mo_3S_{13}]$ (a), $Mo_3S_7Br_4$ (b), $[Mo_3S_7dtc_3]Br$ (c) and $[Mo_3S_4(tu)_8(H_2O)]Cl_4$ (d)
Experimental X-ray emission and XANES spectra of molybdenum and sulfur atoms in a single energy scale for complexes $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]$ and $[\text{Mo}_3\text{S}_4(\text{tu})_8(\text{H}_2\text{O})]\text{Cl}_4$
Conclusions

• Using of X-ray spectroscopy and quantum-chemical methods allowed to study features of the electronic structure of binuclear and trinuclear clusters of transition metal with disulfide ligands.

• The binding energy shifts of the S2p level for disulfide groups is associated with the degree of covalency of the Mo — S bond. Terminal disulfide ligands have the lowest binding energy, which is associated with a weak interaction with a metal atom. In the case of apical disulfide group, it corresponds to the strong covalent interaction of these groups with metal atoms.

• Based on theoretical calculations of the electronic structure of the studied complexes, model XES and NEXAFS spectra of sulfur and molybdenum atom were constructed, which provide information on the contributions of S3p-AO and Mo4d-AO to the HOMOs and LUMOs of complexes.
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Thanks for your attention