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$(NH_4)AgMoS_4$: Synthesis, Structure and Catalytic Activity

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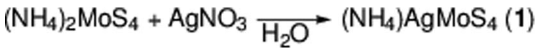
Abstract. The synthesis, characterization and crystal structure of $(NH_4)AgMoS_4$ is presented. $(NH_4)AgMoS_4$ was prepared by the stoichiometric reaction of $AgNO_3$ with $(NH_4)_2MoS_4$. The black microcrystalline $(NH_4)AgMoS_4$ is thermally unstable and contaminated by a phase that analyzes for Ag_2MoS_4. In the TGA continuous weight loss was observed corresponding to the loss of ammonia gas subsequent loss of sulfur and H_2S to give Ag_2S and MoS_2. In the infrared spectrum of $(NH_4)AgMoS_4$, characteristic bands for the ammonium ion at 1350–1400 cm^{-1} and for the $[MoS_4]^{2-}$ group at 460 cm^{-1} are observed. Crystals of $(NH_4)AgMoS_4$ were investigated using a synchroton source. $(NH_4)AgMoS_4$ is isostructural to $(NH_4)CuMoS_4$ and crystallizes in the tetragonal space group $I\bar{4}$ (Z = 2, a = 7.8740(3), c = 5.7733(4) Å). $(NH_4)AgMoS_4$ can be used as a catalyst in the syngas conversion to higher alcohols with showing good activity and ethanol selectivity.

Introduction

Thiomolybdates have been studied extensively with a focus on bioinorganic chemistry,[1–4] heterogeneous catalysis,[5,6] and coordination chemistry.[7] Their importance as lubricants is probably the most widely known property of molybdenum sulfides that is a direct consequence of the low-dimensional structures usually found within this class of compounds.[8,9] Over the last three decades significant progress has been made in synthetic and structural thiometalate chemistry.[10] Particularly, tetrathiomolybdates and tetrathiotungstates are good precursors in the synthesis of transition metal sulfides.[11] The fact that both molybdenum and sulfur can exist in various oxidation states, led to a variety of molecular thiomolybdate species.[1,4,7,12] Only a few polymeric structures have been solved by single crystal structure analysis containing coinage metal cations, forming extended structured with the thiometallate anions.[10,13–17] The growing number of compounds available allows a systematic screening of thiometallates as hydrodesulfurization and hydrodenitrogenation catalysts as well as in higher alcohol synthesis (HAS) from syngas. The latter is a crucial process to meet the increasing demand of ethanol as additive to conventional gasoline, as chemical feedstock and as hydrogen carrier. The historic and current developments of this ongoing search for an efficient catalytic process for the conversion of syngas to ethanol have recently been published in a comprehensive review.[18] Here, as a contribution to this search we present a case study of the metal thiomolybdate $(NH_4)AgMoS_4$, its synthesis, structural analysis and preliminary results of catalytic activity in HAS.

Results and Discussion

For the catalytic screening of late transition metal thiomolybdates in HAS, $(NH_4)AgMoS_4$ (**1**) was prepared from the stoichiometric reaction between $AgNO_3$ and $(NH_4)_2MoS_4$ (Scheme 1).[19]



$$(NH_4)_2MoS_4 + AgNO_3 \xrightarrow[H_2O]{} (NH_4)AgMoS_4\ (\mathbf{1})$$

Scheme 1. Synthesis of **1**.

The presence of silver, molybdenum and sulfur in **1** was confirmed by EDS (Supporting Information). The infrared spectrum of **1** showed characteristic bands for the ammonium ion at 1350–1400 cm^{-1} and for the $[MoS_4]^{2-}$ group at 460 cm^{-1} (Figure 1).[19] In the TGA continuous weight loss was observed possibly corresponding to the loss of ammonia gas until 170 °C and subsequent loss of sulfur and H_2S to give Ag_2S and MoS_2 until 400 °C (Figure 1). The instability of $(NH_4)AgMoS_4$ in heating is attributed to the release of NH_3 and the transfer of a proton to a sulfide ion. The elimination of H_2S is also accompanied by internal redox chemistry that converts the Mo^{6+} to Mo^{4+} that leads to the formation MoS_2.

The structural characterization of $(NH_4)AgMoS_4$ (**1**) was initially carried out by powder diffraction (Figure 1).

The diffraction patterns showed **1** to be isostructural to $(NH_4)CuMoS_4$.[19] The characterization of **1** by single crystal X-ray diffraction was very challenging because of the intrinsic tendency to crystallize rapidly as microcrystals as soon as the solutions of the reagents are combined. Very tiny black single crystals were structurally characterized using synchrotron radi-

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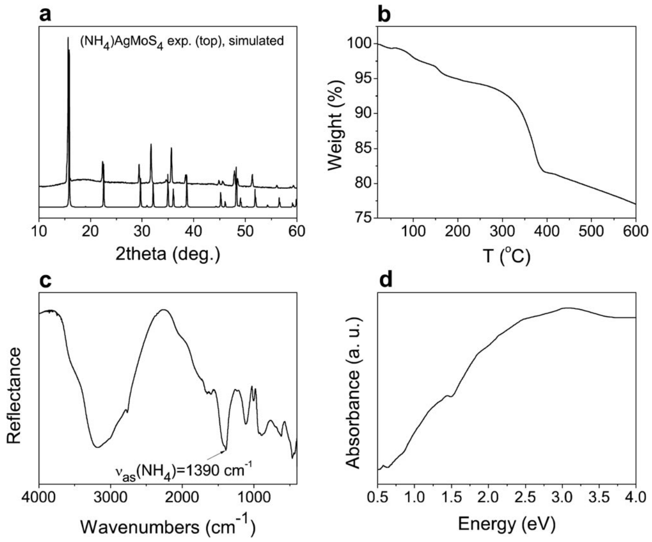

Figure 1. a) Simulated and experimental powder X-ray diffraction pattern of **1**. b) Thermogravimetric analysis of **1** (heating rate 10 K·min^{-1} under nitrogen flow 30 mL·min^{-1}). c) Infrared spectrum of **1** showing the characteristic N–H band at 1390 cm^{-1} and the Mo–S band at 460 cm^{-1}. d) Solid-state UV/Vis optical absorption spectra of **1** (converted from reflectance) showing a band gap of ca. 0.7–1 eV.

ation (Advanced Photon Source, Argonne National Laboratory). Compound **1** crystallizes in the tetragonal space group *I*$\bar{4}$. The compound is isostructural to the previously reported salts $(NH_4)MWS_4$ (*M* = Cu, Ag) and $(NH_4)CuMoS_4$.[15, 19, 20] The main structural features of **1** are the 1D arrangement of $[AgMoS_4^-]_n$ units consisting of tetrahedrally coordinated silver and molybdenum atoms (Figure 2). A detailed structural discussion has been published for $(NH_4)MWS_4$ (*M* = Cu, Ag) and $(NH_4)CuMoS_4$.[15,19,20] The material absorbs light over a wide range of the spectrum include the entire visible spectrum, Figure 1(d). This strong absorption is not found in the single $[MoS_4]^{2-}$ ion and is attributed to intense charge transfer transitions from sulfur based orbitals to silver and molybdenum based orbitals.

Having characterized **1**, the catalytic properties of **1** in the syngas conversion to higher alcohols (higher alcohol synthesis, HAS) were determined (Table 1). It is noteworthy that the overall catalyst performance is similar to other previously investigated transition metal thiomolybdate catalysts.[18] Also desirable conversions > 10 % with good ethanol and propanol selectivities were obtained at temperatures below 350 °C.[21]

Table 1. Conversion of Syngas on $(NH_4)AgMoS_4$ catalyst.

T /°C	Conv. /%	CO_2-free Selectivity /%				
		CH_4	C_2–C_6 HC	MeOH	EtOH	*n*-PrOH
300	4.8	17	3.3	53	21	3.8
320	9.2	28	4.7	42	23	4.8
340	16	31	8.0	30	22	6.2
360	25	38	13	15	21	9.1

The MoS_2 (DOW Chemical) catalyst, however, remains the benchmark in the direct conversion of syngas to higher alcohols with higher CO conversion (29.2 at 295 °C) and higher ethanol selectivity 40.7 %.[22] $(NH_4)AgMoS_4$ (**1**) in comparison shows ethanol selectivity of ca. 20 % in the investigated temperature range of 300–360 °C with a maximum CO conversion of 25 % at 360 °C.

In summary, the synthesis, characterization and investigation of the new compound $(NH_4)AgMoS_4$ (**1**) are reported along with preliminary results on the catalytic performance in higher alcohol synthesis. The data indicates that decomposition of crystalline chalcogenido molybdates into metal sulfides and MoS_2 at elevated temperatures could produce a family of improved MoS_2-based catalysts for higher alcohol synthesis. Further investigations into the influence of the transition metal on selectivity and CO conversion are in progress.

Experimental Section

$(NH_4)_2MoS_4$ (**1**) was synthesized according to a published procedure.[11] The preparation of $(NH_4)AgMoS_4$ was performed in a nitrogen-filled glovebox. $(NH_4)_2MoS_4$ (2.08 g, 8.00 mmol) was dissolved in H_2O (40 mL) to give a dark red solution. Upon addition of a solution of $AgNO_3$ (1.36 g, 8.00 mmol) in H_2O (25 mL), a black precipitate formed immediately suspended in a dark red solution. The mixture was stirred for 1 h. The product was filtered and washed, first with

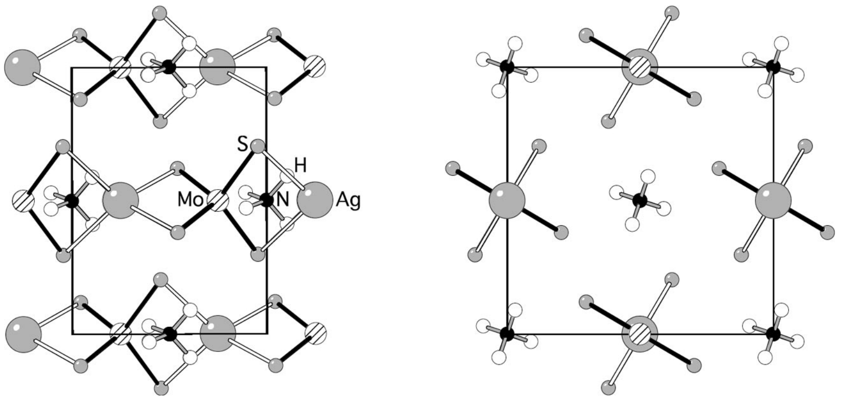

Figure 2. Structure of $(NH_4)AgMoS_4$ (**1**) in the solid state. Unit cell diagram in [010] (left) and [001] (right) direction. Selected bond lengths / Å and angles /°: Mo–S 2.2047(8), Ag–S 2.5158(8), Ag–Mo 2.8867(2), S–Mo–S^{i} 106.91(2), S^{i}–Mo–S^{ii} 114.73(4), S^{iv}–Ag–S^{i} 117.09(2), S^{iv}–Ag–S^{v} 95.12(4), Mo–S–Ag^{iii} 75.08(3). Symmetry labels i $-y+1/2$, $x+1/2$, $-z+1/2$; ii $y-1/2$, $-x+1/2$, $-z+1/2$; iii x, y, $z-1$; iv $-x$, $-y+1$, $z+1$; v x, y, $z+1$.

water (40 mL), subsequently with EtOH (15 mL) and with diethyl ether (10 mL). The microcrystalline compound was dried under reduced pressure overnight. Yield: 1.95 g (70 %) (NH_4)$AgMoS_4$. The presence of silver, molybdenum, and sulfur was confirmed by semiquantitative energy dispersive X-ray analysis (EDS) with a Hitachi S-3400 scanning electron microscope (SEM) equipped with a PGT energy dispersive X-ray analyzer. Found: S 67.4, Mo14.4, Ag 18.2 at.-%. Single-crystalline needles of (NH_4)$AgMoS_4$ are contaminated by tiny amounts of amorphous Ag_2MoS_4 and possibly Ag_2S. EDX of the contaminant: Found: S 59.6, Mo10.4, Ag 30.0 at.-%. Powder X-ray diffraction (PXRD) analyses were performed using an INEL CPS120 powder diffractometer (flat geometry) with graphite monochromatized Cu-K_α radiation. Infra-red spectra of solid samples were obtained with a Thermo Nicolet 6700 FT-IR spectrometer. Spectra were obtained on fine powders in diffused reflectance mode under nitrogen atmosphere and averaging 256 interferograms with resolution of 2 cm^{-1}. The TGA measurements were performed on a Shimadzu TGA-50 thermogravimetric analyzer in aluminum boats under N_2 flow (30 $mL\cdot min^{-1}$). UV/vis diffuse reflectance spectra were recorded at room temperature with a Shimadzu model UV-3101PC double-beam, double monochromator spectrophotometer as described elsewhere.[23] Details of the single crystal structure refinement of (NH_4)$AgMoS_4$ and coordinates are listed in Table 2 and Table 3.

Table 2. Details of the X-Ray Data Collection and Refinement for (NH_4)$AgMoS_4$ (**1**).

	1
formula	NH_4AgMoS_4
formula weight	350.09
T /K	100(3)
crystal system	Tetragonal
space group	$I\bar{4}$
a /Å	7.8740(3)
c /Å	5.7733(4)
V /Å^3	357.94(3)
Z	2
ρ /g·cm^{-3}	3.248
μ /mm^{-1}	8.433
F(000)	328
reflections collected	5408
unique data	1258
R_{int}	0.0380
parameters	20
R_1[a] [$I>2\sigma(I)$]	0.0284
wR_2[b]	0.0707

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, b) $wR_2 = \{\Sigma[w(|F_o|^2-|F_c|^2)^2]/\Sigma[w(|F_o|^4)]\}^{1/2}$.

Table 3. Atomic coordinates and equivalent isotropic displacement parameters /Å^2 for (NH_4)$AgMoS_4$ (**1**).

Label	x	y	z	U_{eq}*
Mo	0	0.5	0.25	0.00503(7)
Ag	0	0.5	0.75	0.01325(9)
S	0.11944(11)	0.29670(11)	0.04406(14)	0.01169(13)
N	0.5	0.5	0	0.0252(15)
H	0.411(6)	0.470(8)	0.106(9)	0.025

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

The activity of the catalysts for higher alcohol synthesis from CO and H_2 mixtures was evaluated in a high pressure (100 atm), stainless steel tubular reactor system. Prior to testing, sulfide samples were physically mixed 10 wt.-% potassium carbonate, pressed, and sized to 0.2–0.5 mm particle sizes. These particles (1.5 g) were diluted with an equal volume of 0.2–0.5 mm quartz chips and loaded in 3 mm internal diameter stainless steel tubing heated within an aluminum block heater. A feed mixture consisting of CO, H_2 and N_2 gases at a fixed ratio of 47.5, 47.5 and 5 v/v % respectively was provided from compressed gas cylinders (Airgas, UHP grade) with flows controlled by Brooks digital mass flow controllers at a total flowrate of 300 sccm. An activated carbon trap was used in the line to trap any undesired iron carbonyl species, which may originate from the CO cylinder. The reaction products were analyzed using a Siemens MAXUM gas chromatograph with a Reoplex precolumn to separate oxygenates and hydrocarbons connected in series with a Porapak QS column and a Molsieve 5 Å column to separate the fixed gases.

X-ray Crystallographic Study

Data for **1** was collected with a Bruker Smart Apex II diffractometer using synchrotron radiation (Advanced Photon Source, Argonne National Laboratory; $\lambda = 0.4428$ Å). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 (all data) using the SHELXTL program package.[24] **1** was refined as a racemic twin (BASF = 0.50481). Hydrogen atoms were refined with a fixed bond length of 0.96 Å using the DFIX instruction, non-hydrogen atoms were assigned anisotropic thermal parameters. A summary of crystal data and refinement parameters is given in Table 2. Atomic coordinates are listed in Table 3.

Supporting Information (see footnote on the first page of this article): Details of the EDX analysis of compound **1** and the amorphous byproduct.

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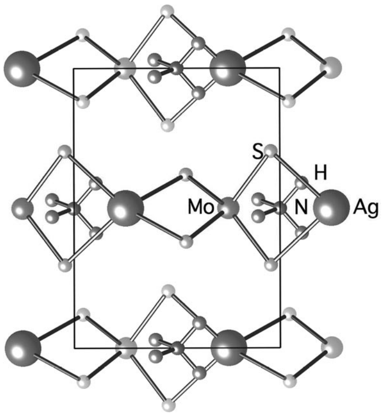
S
H
Mo
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Ag