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# FTIR study of unsupported molybdenum sulfide - *in situ* synthesis and surface properties characterization

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## ABSTRACT

Self-supporting molybdenum sulfide samples with high surface area were prepared by *in situ* thermal decomposition in vacuum of ammonium thiomolybdate. BET specific surface area of the resulting material has its highest values of about 120 m<sup>2</sup>/g for samples treated *in situ* at 473 K and decreases on further heating, while the composition of samples treated at 423 - 473 K is close to MoS<sub>3</sub>, and after heating up to 573 K corresponds to MoS<sub>2</sub>. FTIR spectra show that precursor decomposition is almost completed already after treatment at 423 K, although the sample still contains admixed ammonium ions. After 473 K most of contaminations are gone. Spectra of adsorbed NH<sub>3</sub>, ND<sub>3</sub>, CO, SO<sub>2</sub>, CO<sub>2</sub>, COS and CH<sub>3</sub>SH adsorbed on samples pretreated at 423- 473 K are very close to those obtained for air-contacted MoS<sub>2</sub> powder. However higher band intensities and used of labelled compound enabled us to identify the bands of coordinately bonded ammonia and to point to the existence of acidic species able to protonate ammoniac. Molecularly adsorbed CH<sub>3</sub>SH could be distinguished from its dissociative form ; this reveals the existence of acid base pair sites on bulk molybdenum sulfide.

**Key words :** Infrared spectroscopy, ammonium tetrathiomolybdate, MoS<sub>2</sub> , surface sites, acidity, basicity, adsorption.

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## 1. INTRODUCTION

Studies of the surface of unsupported MoS<sub>2</sub> are of a great importance to distinguish the original properties of the catalyst from those induced by the support. Recently [1] a FTIR study of sulfide pressed in self-supported pellets has demonstrated the applicability of transmittance IR spectroscopy for the studies of this material that is transparent enough below 2500 cm<sup>-1</sup>. However, the air contacted sulfide, despite all the precautions, is always partially hydrolysed and oxidised. To remove surface contaminations thermo-evacuation and treatment in H<sub>2</sub>-H<sub>2</sub>S mixture at 673 K were necessary. Specific surface area of such powder is initially comparatively low (56 m<sup>2</sup>g<sup>-1</sup>) and decreases even more during the thermal treatment. Moreover, sulfidation in H<sub>2</sub>-H<sub>2</sub>S mixture causes transparency lowering, making the samples opaque above 2000 cm<sup>-1</sup>.

It was, thus, attractive, to find a way to prepare pellets of disperse sulfide avoiding completely contact with the air after decomposition. Some of disperse oxides, such as CaO, that also are not stable against atmospheric water or CO<sub>2</sub>, could be prepared by decomposition in vacuum of the pellets, preliminary pressed of the hydroxide. Just the same, MgO, NiO, CoO with high surface area could be prepared from corresponding precursors: hydroxides, carbonates, basic carbonates, etc. The pellets normally resist heating and keep their shape, although diminish in dimension. The resulting oxides have very high surface area and contain minimum of surface contaminations, such as OH groups that remain after hydroxide decomposition.

In this work an attempt was undertaken to prepare MoS<sub>2</sub> samples by thermal decomposition of the pellets pressed of ammonium tetrathiomolybdate directly in the IR cell. Pressure monitoring during the heating, BET surface measurements and chemical analysis of the resulting materials after treatment at different temperatures were carried out to follow the decomposition process, and spectral characterisation of pellets using the adsorption of different test molecules had to provide information about the changes in surface properties of the sulfide phase.

## 2. EXPERIMENTAL

The earlier described [2] IR cell for low-temperature studies at 60–300 K was equipped with ZnSe inner windows that combined with the exterior windows of KBr enabled the spectra to be registered up to about  $600\text{ cm}^{-1}$ . The cell was connected to a vacuum line that provided pumping at  $10^{-6}$  Torr. The pressure of the adsorbed gases could be measured by two Barocel gauges, the more precise one attached directly to the sample-containing compartment of the cell. Another one was used to measure a dose of gas in the known volume before letting it into the cell. The sample temperature during the treatment or recording the spectra was monitored by a chromel–alumel thermocouple inserted into the heater or into the coolant compartment of the cell. For spectra registration at low temperatures, about 0.5 Torr of He was added into the cell to achieve better thermal contact of the pellet with the inner part of the cell. Then, if liquid nitrogen was used as a cooling agent, the temperature of the sample did not differ from 77 K more than by 5 K.

Batches of about 20 mg of ammonium tetrathiomolybdate (99.97% purity, from Aldrich Chem. Co) were pressed into  $2\text{ cm}^2$  self-supporting pellets. The BET specific surface area measurements were carried out with the use of nitrogen adsorption at 77 K on the samples evacuated for 1h at 423, 473, 573 or 673 K. Chemical quantitative analysis of pellets evacuated at 423, 473 and 573 K has been proceeded by direct combustion and IR detection of  $\text{SO}_2$  for sulfur and by inductive plasma analysis (ICP) for Mo in the Service Central d'Analyse du CNRS.

For FTIR measurements pellets of ammonium tetrathiomolybdate were placed in the cell and carefully heated in vacuum with a rate of about 4 K/min. up to the desired temperature, typically 423, 473 or 573 K. Simultaneous pressure measurements enabled us to follow the process of decomposition. Normally, heating in vacuum does not destroy the pellets, that instead of initial dark-red colour become black. After evacuation for 1-2 h at the desired temperature samples were cooled up to 300 or 77 K and adsorption of different molecules could be studied.

Commercial  $\text{NH}_3$ ,  $\text{ND}_3$  (99.75% of isotopic purity),  $\text{H}_2\text{S}$ ,  $\text{H}_2$ ,  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{COS}$  and  $\text{CH}_3\text{SH}$  were used. Spectra of adsorbed ammonia and  $\text{CH}_3\text{SH}$ , were studied at 190-300 K, those of CO were registered at 77 K.  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{COS}$ , and  $\text{H}_2\text{S}$  were usually added at 77 K and first condensed on the cell walls. Then liquid nitrogen was removed and the cell was let to warm up to certain temperature, depending on the adsorbate, until the pressure increase and the appearance of new bands in the spectrum indicate surface saturation with the adsorbed molecules. Then, the cell was cooled again and spectra were measured at 77 K. To follow the desorption, the sample was just moved for certain time into the quartz tube normally used for the thermovacuum treatment, that could be at 300 K or any desired temperature. The desorbing

molecules were trapped on the frozen walls of the cell and one could follow the process up to complete desorption of the adsorbed species.

FT-IR spectra were recorded with a ThermoNicolet NEXUS FT-IR spectrometer equipped with an MCT-A detector cooled with liquid nitrogen that enabled us to register the bands with a reasonable signal-to-noise ratio for the absorption up to three units. For the 650–600  $\text{cm}^{-1}$  region, a DTGS detector was used. The spectrometer operated at 4  $\text{cm}^{-1}$  resolution collecting typically 512 scans.

### 3. RESULTS

#### 3.1. Decomposition of ammonium tetrathiomolybdate and ammonia adsorption

Pressure measurements during sample treatment in the IR cell show almost no gas emission up to 393 K. Then, the decomposition starts, that has a maximum rate at about 423K, and is completed at about 443 K. If the temperature increase is stopped at 423 K and the sample is kept at this temperature for 1-5 h, further heating up to 473 K does not lead to noticeable pressure increase, thus showing that most of the precursor is decomposed in these conditions.

Table 1. Conditions of thermovacuum treatment, results of weight loss and surface area measurements and chemical analysis data for the samples obtained by molybdenum thiomolybdate decomposition.

Pretreatment conditions		Weight loss,%	BET surface area, $\text{m}^2/\text{g}$	x in $\text{MoS}_x^*$
T, K	Time, h			
423	5.5	23.8	118	2.9
473	1	25.7	121	3.3
573	1	26.1	59	2.0
673	1	27.6	35	

\* content of S in gramm-atoms found from chemical quantitative analysis of samples related to that of Mo.

The results of specific surface area measurements and chemical analysis of the material after thermovacuum treatment at different temperatures are summarized in Table 1. The presented data infer that the formation of molybdenum sulfide material with high surface area is practically completed after heating at 423 K. Small increase of the area observed after heating up to 473 K could be explained by the loose of mass due to desorption of residual ammonia or  $\text{H}_2\text{S}$ , evidenced by the weight loss measurements data (see Table 1). At this stage the composition of the sample is close to  $\text{MoS}_3$ . Further heating up to 573 K, according to the results of chemical analysis, leads to the conversion of  $\text{MoS}_3$  to  $\text{MoS}_2$ . Elimination of sulfur does not, however, lead to the surface increase, but on the contrary, causes its two-fold diminution. The sintering, evidenced by the decrease of surface area, continues when the temperature of vacuum treatment is raised up to 673 K. After that, a yellow deposit, evidently, of elementary sulfur, could be seen

on the glass walls of the reactor. Unfortunately, the mass of the sulfur deposit could not be measured separately from that of the molybdenum sulfide material, and the weight loss values given in Table 1 for 573 - 673 K do not reflect sulfur elimination.

FTIR spectra changes observed during thiomolybdate decomposition are illustrated in Fig.1. The initial pellet is completely opaque in 3420 - 2720  $\text{cm}^{-1}$  and 1700 - 1280  $\text{cm}^{-1}$  regions. Several sharp bands could be detected at 1118  $\text{cm}^{-1}$  and below (curve 1). Evacuation at 300-373 K does not cause any changes in the spectrum, except of disappearance of a shoulder at about 3540  $\text{cm}^{-1}$ , evidently due to the removal of molecular water. After evacuation at 423 K, however, spectrum changes completely. Absorption is complete above 3000  $\text{cm}^{-1}$ , weakens with the frequency decrease, and below 2200  $\text{cm}^{-1}$  becomes lower than 3. Several bands could be seen in the spectrum of such sample (curve 2) at 1705, 1585, 1400, 1230, 1028 and 958  $\text{cm}^{-1}$ . After heating up to 473 K most of them are gone or strongly diminish in intensity except of the last one that in accordance with earlier studied molybdenum sulfide [1] should be associated with the admixed Mo=O groups on the sulfide surface. Subsequent ammonia addition restores partially the intensity of bands at 1585 and about 1230  $\text{cm}^{-1}$ , one more band grows at 1440  $\text{cm}^{-1}$ . This shows that these bands could be due to certain quantity of residual ammonia or ammonium ions still remaining in the sample after decomposition of thiomolybdate.

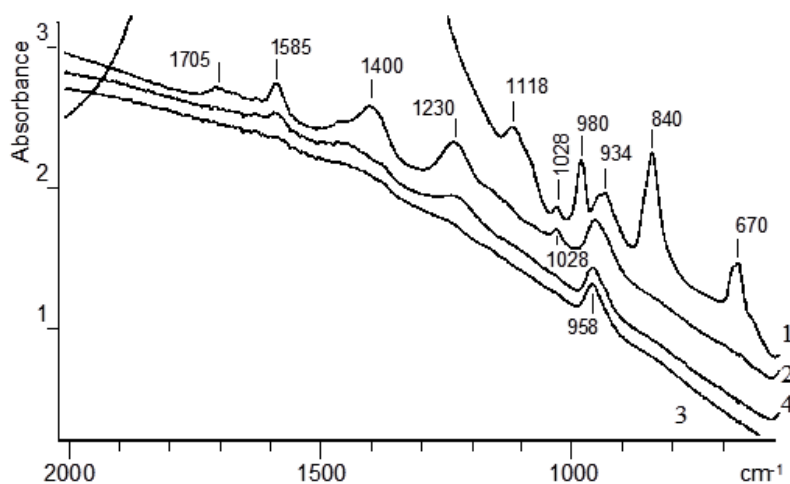


Fig 1. FTIR spectrum of ammonium thiomolybdate pellet ( $12 \text{ mg/cm}^2$ ) outgassed at 300 K (1), 423 K (2), 473 K (3), and after addition of up to 1 Torr of ammonia (4).

In more detail the data on ammonia interaction with the  $\text{MoS}_2$  prepared from thiomolybdate *in situ* decomposition up to 473 K are presented in Fig. 2. Curve 1 shows a difference between the spectra of adsorbed ammonia and of the sample outgassed at 473 K before adsorption given in Fig 1, curves 4 and 3, respectively. Besides the mentioned bands at 1585, 1440 and 1215  $\text{cm}^{-1}$ , at least two more bands could be distinguished at 1375 and 1105  $\text{cm}^{-1}$ . Subsequent evacuation (curve 2) reveals dissimilarity in the stability of different forms of

adsorbed ammonia. Bands at 1440 and 1105  $\text{cm}^{-1}$  disappear completely after short evacuation, those at 1585 and 1215  $\text{cm}^{-1}$  diminish substantially, while the 1375  $\text{cm}^{-1}$  band seems not to change at all.

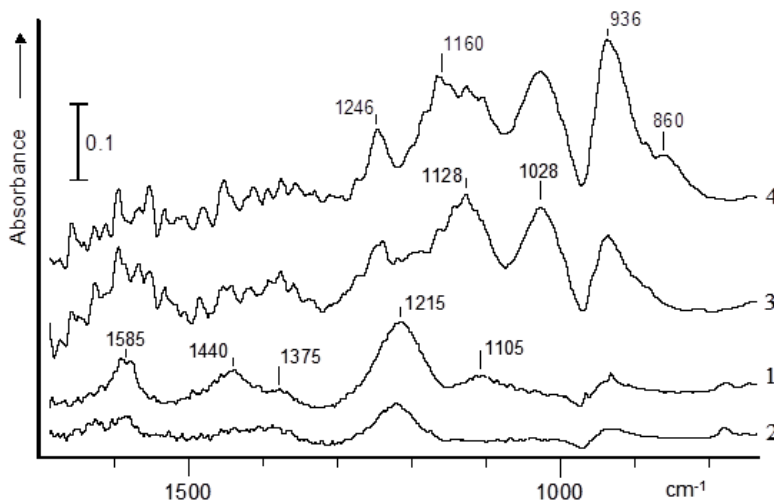


Fig. 2. FTIR spectrum of  $\text{NH}_3$  and  $\text{ND}_3$  adsorbed on molybdenum sulfide obtained by *in situ* decomposition of ammonium thiomolybdate at 473 K. 1-after addition of  $\text{NH}_3$  (1 Torr), 2-subsequent evacuation for 5 min, 3-adsorption of  $\text{ND}_3$  (1 Torr) on a fresh sample, 4- after evacuation and addition of a new dose of  $\text{ND}_3$  (13 Torr). Spectra of samples before adsorption are subtracted.

Addition of small doses of  $\text{ND}_3$  results first in the appearance of the same bands as after  $\text{NH}_3$  adsorption, evidently due to the exchange with the proton-containing species on the walls of the system and on the sample surface. However, after admitting several Torr of  $\text{ND}_3$  (curve 3) bands at 1246, 1160, 1128, 1028, 936 and 860  $\text{cm}^{-1}$  arise. Repeated pumping and addition of new portions of gas (curve 4) lead to intensity redistribution with the preferential growth of the maximum at 936  $\text{cm}^{-1}$ . Removal of the gas phase results in the disappearance of the bands at 1160 and 860  $\text{cm}^{-1}$ .

### 3.2. Adsorption of $\text{CH}_3\text{SH}$

The results on  $\text{CH}_3\text{SH}$  adsorption are in accordance with the earlier data [1] although providing more detailed information that enable us to distinguish between the weakly adsorbed and chemisorbed species. Fig. 3 shows the spectra obtained after  $\text{CH}_3\text{SH}$  adsorption at 300 K on a sample pretreated at 423 K and after cooling the sample down to 190 K, that results in a great intensity increase of the bands, observed at 1428, 1319, 1060, 958, 801 and 700  $\text{cm}^{-1}$  (curve 1). Removal of the adsorbate at progressively increasing temperatures reveals different stability of the bands. While those at 1319, 1060, 801 and 700  $\text{cm}^{-1}$  start to decrease after freezing the adsorbate vapour in the presence of helium already at 200 K (curve 2) and disappear completely after pumping at 260 K (curve 5), bands at 1428, 958  $\text{cm}^{-1}$  although diminish and move slightly

to lower wavenumbers ( $1414$  and  $951\text{ cm}^{-1}$ ), remain in the spectrum up to  $290\text{ K}$  (curve 7) together with the band at  $1299\text{ cm}^{-1}$ , whose intensity seems not to change almost at all during all the treatment. We can, thus, attribute the latter three bands to somehow chemisorbed species, while those at  $1428$ ,  $1319$ ,  $1060$ ,  $958$ ,  $801$  and  $700\text{ cm}^{-1}$ - to weaker molecular adsorption. Overlapping of the  $1428$  and  $958\text{ cm}^{-1}$  bands with closely located bands of chemisorbed species does not enable us to follow separately their intensity changes, but the difference in the peak positions and thermal stability unambiguously point to the coexistence of two surface species with partially superimposed absorption bands.

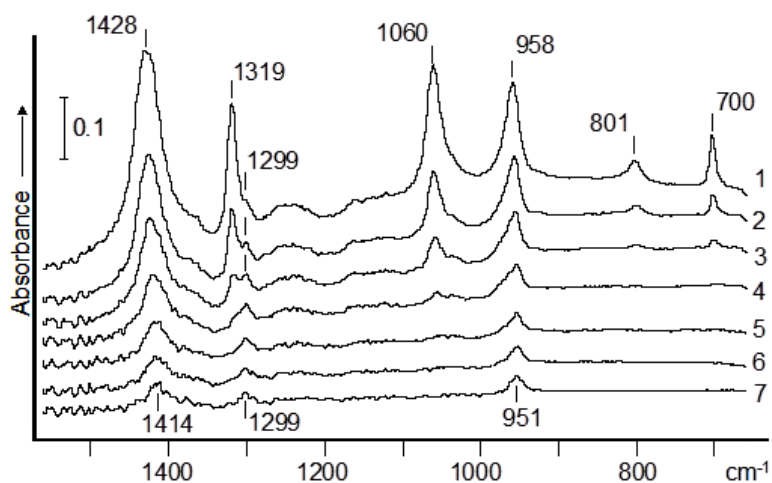


Fig. 3. FTIR spectrum of  $\text{CH}_3\text{SH}$  adsorbed on molybdenum sulfide obtained by *in situ* decomposition of ammonium thiomolybdate at  $423\text{ K}$ . 1-after addition of  $\text{CH}_3\text{SH}$  ( $7.5\text{ Torr}$ ) and cooling down to  $190\text{ K}$ , 2-after removal of adsorbate vapour by freezing at  $200\text{ K}$ , 3-  $220\text{ K}$ , 4- at  $240\text{ K}$ , 5- after pumping for  $30\text{ min}$  at  $260\text{ K}$ , 6- at  $273\text{ K}$  and 7- at  $286\text{ K}$ . Spectrum of the sample before adsorption is subtracted.

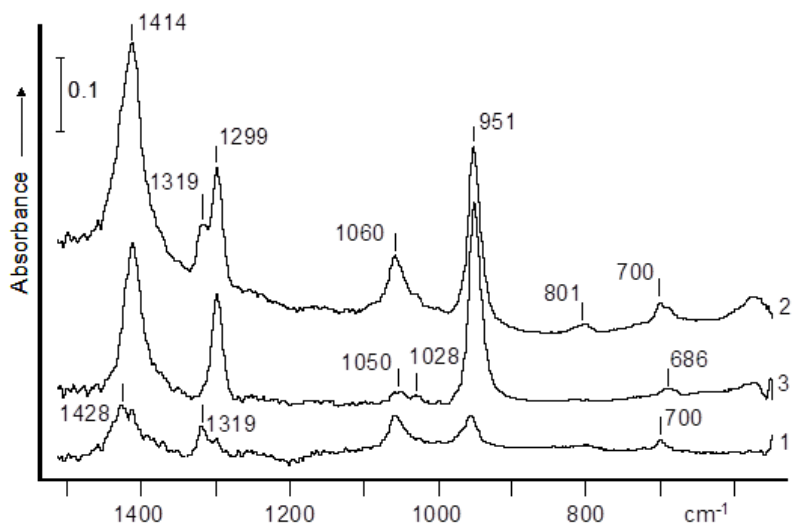


Fig.4. FTIR spectrum of  $\text{CH}_3\text{SH}$  adsorbed on molybdenum sulfide obtained by *in situ* decomposition of ammonium thiomolybdate at  $423\text{ K}$ . 1- after addition of  $\text{CH}_3\text{SH}$  ( $7.5\text{ Torr}$ ) 2-after heating in the presence of  $40\text{ Torr}$  of  $\text{CH}_3\text{SH}$  at  $393\text{ K}$  for  $30\text{ min}$ ., 3- after  $30\text{ min}$ . more in  $\text{CH}_3\text{SH}$  and pumping off at  $393\text{ K}$  for  $20\text{ min}$ . Spectrum of the sample before adsorption is subtracted.

Heating of the sample in CH<sub>3</sub>SH vapour up to 393 K (Fig. 4, curve 2) causes a tremendous intensity increase of the bands of chemisorbed species and makes visible less intense bands at 1050, 1028 and 686 cm<sup>-1</sup>. After pumping off the gas of the cell only bands of this compound remain in the spectrum of adsorbed CH<sub>3</sub>SH (curve 3). Evacuation at 423 K does not affect the spectrum, but after heating in vacuum at 473 K for 30 min all the bands of chemisorbed CH<sub>3</sub>SH disappear. Spectral data on CH<sub>3</sub>SH adsorption, together with the frequencies of free molecule in gas phase with their assignment according to [3], are summarized in Table 2.

Table 2 Frequencies and assignment of the bands in IR spectra of CH<sub>3</sub>SH in gas [3] and adsorbed on molybdenum sulfide obtained by ammonium thiomolybdate decomposition at 423 K

Mode number	Assignment	IR, gas [3]	Weak ads.	Strong ads.
1, 9	C-H	3000	*	*
3	S-H	2597	*	*
4	HCH	1475	-	-
10	HCH	1430	1428	1414
5	HCH	1335	1319	1299
11	SCH	1074	1060	1050
6	SCH	976	958	951
7	CSH	803	801	-
8	C-S	708	700	686

\* region closed by the bulk absorption of sulfide

### 3.3. Adsorption of CO, CO<sub>2</sub>, COS, CS<sub>2</sub> and SO<sub>2</sub>

CO adsorption at 77 K on the sample pretreated at 423 K, the most transparent in that spectral region (Fig. 5), leads to the band at 2135 cm<sup>-1</sup>, accompanied by a shoulder at about 2165 cm<sup>-1</sup> and a broad band centered at 2100 cm<sup>-1</sup> that becomes more intense after heating the sample up to 300 K in CO by moving it for about one min. into the warm part of the cell. The observed meanwhile pressure increase enables an estimate to be made of the surface coverage by CO. At a pressure of 6.3 Torr it turns to be close to a monolayer. The shoulder at 2165 cm<sup>-1</sup> disappears immediately after pumping off the gas phase. Evacuation for 1-3 min enhances sample heating by the beam, before gaseous He is newly admitted. In this conditions the band at 2135 cm<sup>-1</sup> disappears. Broad band at 2100 cm<sup>-1</sup> is the last one to be removed after longer evacuation. These data are in accordance with the earlier observed [1] spectra of CO adsorbed on oxidized unsupported MoS<sub>2</sub> treated at 673 K. One can only note that the most sTable form in that case [1] had somehow lower position, at 2086-2070 cm<sup>-1</sup>.

In the spectrum of CO<sub>2</sub> adsorbed at about 120 K on the sample pretreated at 423 K, besides the earlier observed [1] band that shifts with the decreasing coverage from 2331 to 2326 cm<sup>-1</sup>, the band of bending vibration mode was detected, that also moves slightly from 656 to 653 cm<sup>-1</sup>

with the decreasing amount of adsorbed molecules. The bands are not visible in the presence of gas at 300 K, but appear after cooling up to at least 220 K. Bands of COS adsorbed on the same sample at 200 K were detected at 2038 and 854  $\text{cm}^{-1}$ , the more intense former one could be seen at 273 K, and disappear after pumping at ambient temperature. The only intense band of  $\text{CS}_2$  was observed at 1503  $\text{cm}^{-1}$  in the presence of adsorbate at 200-273 K, it disappears after pumping off for 20 min at 273 K.

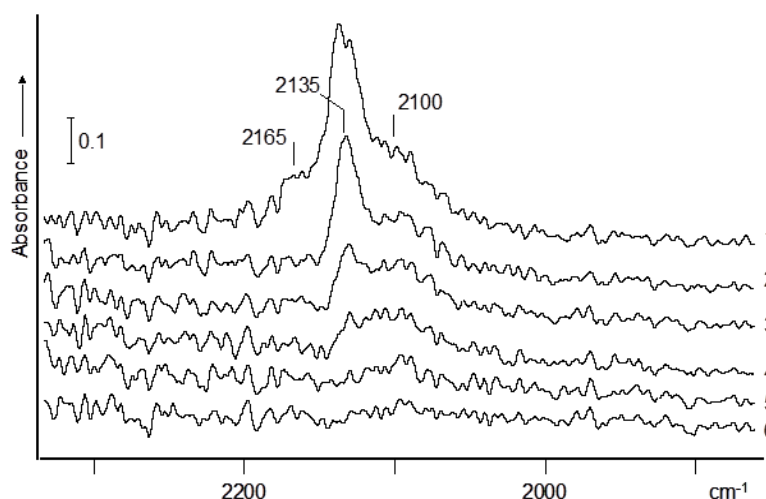


Fig 5. FTIR spectrum of CO adsorbed at 77 K on molybdenum sulfide obtained by *in situ* decomposition of ammonium thiomolybdate at 423 K. 1- in the presence of CO gas (6.3 Torr); 2 - 6 after evacuation for progressively increasing time (0.5, 1.0, 1.5, 3 and 5 min., respectively), followed by addition of He. Spectrum of the sample before adsorption is subtracted.

$\text{SO}_2$  addition at ambient temperature results in a band at 1331  $\text{cm}^{-1}$  and less intense one at 1140  $\text{cm}^{-1}$ . After cooling the cell up to 200 K their intensities increase greatly. Heating in the presence of  $\text{SO}_2$  gas does not lead to any other bands. Positions of the bands in the spectra of adsorbed CO,  $\text{CO}_2$ , COS,  $\text{CS}_2$  and  $\text{SO}_2$  are summarized in Table 3.

Table 3. Vibrational frequencies of CO,  $\text{CO}_2$ , COS,  $\text{CS}_2$  and  $\text{SO}_2$  in gas phase [4], adsorbed on molybdenum sulfide\* obtained by ammonium thiomolybdate decomposition at 423 K, and on unsupported  $\text{MoS}_2$  [1] (in the brackets).

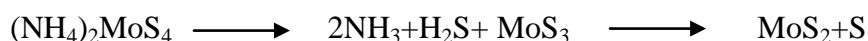
CO		$\text{CO}_2$		COS		$\text{CS}_2$		$\text{SO}_2$	
Gas	Ads.	Gas	Ads.	gas	Ads.	Gas	Ads.	Gas	Ads.
2143	2165 (2157)	2349	2326 (2326)	2062	2038 (2032)	1533	1503	1351	1331 (1327)
	2135 (2134)	1337		859	854 (857)	658		1147	1140 (1141)
	2100 (2186, 2170)	667	653	520		397		517	

\*For bands whose position changes with coverage, the most shifted values are given, that correspond to the lowest coverages

#### 4. DISCUSSION

Combination of FTIR spectral study with BET measurements and chemical analysis provides a better understanding of the mechanism of thiomolybdate decomposition and molybdenum sulfide formation. Strong absorption, that makes the sample of initial material opaque in the 3420-2720  $\text{cm}^{-1}$  and 1700- 1280  $\text{cm}^{-1}$  regions is, evidently, due to ammonium ions. Only traces of this absorption remain after evacuation at 423 K accompanied by the pressure increase caused by the emission of gas, apparently, ammonia and  $\text{H}_2\text{S}$ .

Weight loss measurements also testify that the ammonium thiomolybdate decomposition is almost completed at 423 - 473 K. In fact, according to the scheme of this two-step reaction :



After the first stage of gas liberation, a weight loss of 26.1% should be anticipated, while the elimination of sulfur should lead to further increase of this value up to about 38%. This last step could not be observed here, because separate measurement of sulfide and sulfur deposit masses was not possible in our experiments. As seen from the Table 1, the weight loss value corresponding to the first step is achieved after treatment at 573 K. The slightly lower magnitude of 25.7% observed after evacuation at 473 K could be accounted for by the presence of small amount of contaminations, in agreement with IR data of figure 1.

Surface area measurements shows that the molybdenum sulfide formation is practically completed already at 423 K, since the slight surface area increase after treatment at 473 K can be explained by the simultaneously observed mass decrease and related to the removal of surface contaminations. Treatment of the sample at higher temperatures leads to a rapid surface area decrease. According to the results of chemical analysis, the composition of the resulting material pretreated at 423 - 473 K, corresponds to  $\text{MoS}_3$ , while after treatment at 573 K the Mo:S mass ratio finally becomes equal to that expected for  $\text{MoS}_2$ . Yellow deposit on the reactor walls infers that sulfur sublimation from the material indeed takes place at temperatures above 473 K, when the decrease of surface area testify for the sintering process.

Data of FTIR spectroscopy show that after evacuation at 473 K most of contaminations are gone, besides those which account for the band at 958  $\text{cm}^{-1}$  that belongs to Mo=O groups, formed, evidently, as a result of hydrolysis of some part of thiomolybdate in the course of sample preparation. The position of this band is lower than for  $\text{MoO}_3$  film, where it was observed at 990  $\text{cm}^{-1}$  [7], and somewhat higher than for the air-contacted  $\text{MoS}_2$  [1] where an intense band was observed at 940  $\text{cm}^{-1}$  with a shoulder at 960  $\text{cm}^{-1}$ . The 958  $\text{cm}^{-1}$  band is also less intense than the 940  $\text{cm}^{-1}$  band of the air-contacted  $\text{MoS}_2$  sample of the same thickness, evacuated at 673 K. Rough estimation shows that surface concentration of such groups for the material obtained by evacuation at 473 K is about 5 times lower than for  $\text{MoS}_2$  studied in [1]

before sulfidation. Therefore, the *in situ* synthesis of molybdenum sulfide decreases although not completely eliminated the residual oxidic Mo species.

Another dissimilarity between the spectra of the two materials is in the band at  $995\text{ cm}^{-1}$ , observed for the air-contacted  $\text{MoS}_2$  and more intense for the samples that were longer kept in the air. This band, assigned to the  $\text{Mo}^{\text{VI}}=\text{O}$  groups of oxidised layer with oxygen atoms bound to the molybdenum [1], is absent in the spectra of the disperse sulfide. Apparently, the  $\text{Mo}^{\text{IV}}=\text{O}$  groups here are isolated, with only sulfur atoms completing the coordination sphere of molybdenum. This should lead to lower values of the  $\text{Mo}=\text{O}$  frequency, as it was established in the study of  $\text{MoO}_3$  sulfidation [8].

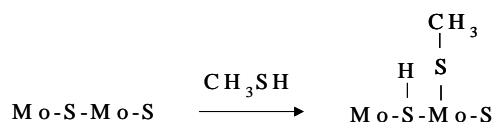
It should also be noted that in the spectrum of the air-contacted  $\text{MoS}_2$  the band at  $940\text{ cm}^{-1}$  was accompanied by a shoulder at  $960\text{ cm}^{-1}$ , that unlike the main peak at  $940\text{ cm}^{-1}$ , was sensitive to adsorption of CO or  $\text{H}_2$  at 77 K. The shoulder was assigned to the  $\text{Mo}^{\text{IV}}=\text{O}$  groups with molybdenum ion with the coordination number lowered with respect to that of the groups which account for the  $940\text{ cm}^{-1}$  band, that enables CO to be bound to such ions. The  $958\text{ cm}^{-1}$  band, observed in this work for the disperse sulfide, does not reveal noticeable sensitivity towards CO adsorption, although its position is very close to the above  $960\text{ cm}^{-1}$  shoulder. We suppose that both the band are due to  $\text{Mo}^{\text{IV}}=\text{O}$  groups with molybdenum ions coordinated to sulfur, however, in the case of Mo sulfide *in situ* synthesized by outgassing at 423-473 K, presence of extra sulfur impedes CO coordination to molybdenum. According to [6], in different possible structures of amorphous  $\text{MoS}_3$ , formed at the first stage of  $(\text{NH}_4)_2\text{Mo}^{\text{VI}}\text{S}_4$  decomposition, part of sulfur in the coordination sphere of molybdenum exists in the form of  $\text{S}_2^{2-}$  ions and not only as  $\text{S}^{2-}$ , like in the case of  $\text{MoS}_2$ , and this we can consider as a possible reason of the small  $\text{Mo}=\text{O}$  frequency difference.

The most intense bands of contaminations in the spectrum of material treated at 423 K coincide with those observed after ammonia adsorption on the same sample outgassed at 473 K, and are close to those obtained for ammonia adsorbed on  $\text{MoS}_2$  [1]. The band at  $1105\text{ cm}^{-1}$  corresponds to weakly bound ammonia observed in [1] at  $1080\text{-}1125\text{ cm}^{-1}$ , depending on coverage. The  $1440\text{ cm}^{-1}$  band was assigned to ammonium  $\text{NH}_4^+$  ions that, depending on the pretreatment conditions had a maximum between  $1490$  and  $1430\text{ cm}^{-1}$  [1]. The assignment of the most stable bands at  $1585$  and  $1230\text{-}1215\text{ cm}^{-1}$  for  $\text{MoS}_2$  was not clear enough. We could not exclude their assignment to the  $\text{NH}_2$  groups, because the position of the  $1585\text{ cm}^{-1}$  band is somewhere between the positions typical of  $\text{NH}_3$  and  $\text{NH}_2$  surface species.

New results of  $\text{ND}_3$  adsorption, presented above in fig. 2 ensure us that the corresponding bands at  $1585$  and  $1215\text{ cm}^{-1}$  of  $\text{NH}_3$  adsorbed on samples evacuated at 473 K are due to strongly held molecular ammonia, most probably, coordinated to Mo ions. In fact, the  $1215\text{ cm}^{-1}$  band

after addition of  $\text{ND}_3$  is split to four peaks at 1215, 1128, 1028 and  $936\text{ cm}^{-1}$  due to the symmetric bending vibration  $\delta_s$  of  $\text{NH}_3$ ,  $\text{NH}_2\text{D}$ ,  $\text{NHD}_2$  and  $\text{ND}_3$  molecules, respectively, that arise as a result of isotopic exchange with proton-containing species on the walls of the system and the cell. Intensity increase of the  $936\text{ cm}^{-1}$  band after repeated addition of new portions of  $\text{ND}_3$  supports this assignment showing that it cannot be the enhanced band of  $\text{Mo}=\text{O}$  groups that occur at almost the same position. The bands at 1246 and  $1160\text{ cm}^{-1}$  observed after  $\text{ND}_3$  adsorption should be due to the asymmetric  $\delta_a$  bending vibration mode of partially and completely substituted ammonia. The frequency ratios observed for the two bending vibrations on deuteraton,  $1585/1160=1.37$  and  $1215/936=1.30$ , are close enough to those of gaseous ammonia:  $1623.7/1191=1.36$  or  $950/747=1.27$ .

Data on methanethiol adsorption reveal the existence of two forms of adsorbed species. The positions of bands of the weakly adsorbed  $\text{CH}_3\text{SH}$  are close to those of gas or liquid phase. Frequency shifts are greater for the chemisorbed methanethiol, and what is the most important, the band at  $801\text{ cm}^{-1}$  is absent at all. This band is due to C-S-H bending vibration, and its absence means that we deal no more with the molecules, but rather with the  $\text{CH}_3\text{S}$  groups, chemically bound to the surface. This explains high thermal stability of the species as well as the activated character of methanethiol adsorption that needs heating up to about 393 K, evidently, to accelerate dissociation. The occurrence of dissociative adsorption of  $\text{CH}_3\text{SH}$  points out the existence of acidic and basic sites on surface molybdenum sulfide. Indeed, the reaction is completely analogous to that of methanol dissociation on oxide surfaces with the formation of methoxy groups and could be represented by the scheme as follows :



Normally, on oxide surfaces several types of methoxy groups could exist that differ in the number of metal atoms bound to oxygen atom of the group and have different positions of the C-O stretching bands [9]. The number of possible structures should be less than the oxygen coordination number in the bulk. Therefore, for  $\text{MoS}_2$  structure with sulfur bound to three Mo atoms one could anticipate the existence of two types of thiolate groups, terminal or bridged that could have slightly different position of the C-S stretching vibration. In fact, the band at  $686\text{ cm}^{-1}$  is not narrow and seems to have a shoulder at about  $692\text{ cm}^{-1}$ , however, the up-to-date data do not enable us to claim definitely about its complex structure.

As could be seen from Table 3, most of the bands of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{COS}$ ,  $\text{CS}_2$  and  $\text{SO}_2$  adsorbed on sulfide samples decomposed at 423 K are shifted significantly, by  $20\text{-}43\text{ cm}^{-1}$ , with

respect to those of gas or liquid. The observed bands, within the limits of their coverage-dependant variations or experimental error, are at the same positions as reported in [1] (in the brackets in Table 1) for unsupported MoS<sub>2</sub>. For metal oxides, CO<sub>2</sub> adsorption on the cations is known to lead to the frequency increase of the  $\nu_{\text{as}}$  stretching vibration. In the case of sulfide the same band is shifted to lower wavenumbers. This could be explained if we assume that adsorption takes place on sulfur anions with a side-on orientation of the adsorbed molecules. In accordance with [1], besides the above mentioned, no other bands that could be due to more complex thiocarbonate-like compounds, were detected.

This is only for CO that the band of the most strongly held molecules at 2100 cm<sup>-1</sup>, reported here for the sample decomposed at 423 K, differs somehow in its position as compared to the earlier studied MoS<sub>2</sub> (2086-2070 cm<sup>-1</sup> [1]). It is noticeable, however, that a band at 2110 cm<sup>-1</sup> with a shoulder at 2070 cm<sup>-1</sup> appeared after low temperature CO adsorption on MoS<sub>2</sub> supported on alumina [10]. In agreement with ab initio calculations [10], CO frequency lowering with respect to the gas phase could be explained by backdonation of d-electrons from the Mo<sup>4+</sup> cation in sulfur environment towards CO molecule. We can suppose that absorption at about 2100 cm<sup>-1</sup> is typical of CO interacting with Mo<sup>4+</sup> cations in a highly dispersed sulfide, where the effect of back-donation is not so strong as in the sintered MoS<sub>2</sub>, although stronger than on the supported MoS<sub>2</sub> phase. Difference of CO band positions between the dispersed and air-contacted sintered MoS<sub>2</sub> does not exceed that one caused by the support, and taking into account high sensitivity of CO to the oxidation state of metal, we can consider these data as an evidence that after decomposition of thiomolybdate at 423 K the molybdenum is already in the 4-valent state.

The position of the 2135 cm<sup>-1</sup> band of weakly held CO is somehow lower than that of gaseous (2143 cm<sup>-1</sup>), liquid or dissolved carbon monoxide and could scarcely be associated with simple physisorption. Electrostatic model of diatomics interacting with ionic surface [11] predicts the side-on adsorption of CO on anions, accompanied with a slight frequency lowering. This should be just a case of adsorption on basal planes of crystalline MoS<sub>2</sub>, where only sulfur anions are available for adsorption, as well as of interaction with amorphous molybdenum sulfide that has the excess of sulfur and a small amount of coordinately unsaturated cations. Quantitative estimations of surface coverage show that in the conditions of the experiment the highest surface coverage was close to the monolayer, that excludes the possibility of all the molecules to interact with the cations. Thus, the side-on adsorption on sulfur anions seems to be quite reasonable explanation of our data on the positions of the 2135 cm<sup>-1</sup> band of CO, as well as of CO<sub>2</sub>, COS and CS<sub>2</sub> that have the same sign of quadrupole momentum.

## 5. CONCLUSIONS

Formation of molybdenum sulfide from ammonium tetrathiomolybdate by its thermal decomposition in vacuum, as well as the adsorption properties of the resulting material have been studied by IR spectroscopy combined with the pressure control, weight loss, surface area measurements and chemical analysis of the product. The pellets of ammonium tetrathiomolybdate were not destroyed by heating in vacuum, and after treatment already at 423 K transform to a black high surface area molybdate samples feasible for infrared studies of adsorption.

According to the weight loss measurements and chemical analysis, the composition of the resulting product obtained at 423 or 473 K is close to  $\text{MoS}_3$ . It is converted to  $\text{MoS}_2$  on further heating up to 573-673K. The surface area of the sulfide, initially as high as  $120 \text{ m}^2/\text{g}$ , decreases dramatically when the transformation to  $\text{MoS}_2$  occurs.

Adsorption properties of the material, obtained after decomposition at 423 K do not differ much from those of unsupported  $\text{MoS}_2$  prepared by the standard method and then evacuated or sulfided in  $\text{H}_2\text{-H}_2\text{S}$  mixture at 400 K. However, higher band intensities in the spectra of this material enable one to obtain more detailed information about the nature of surface species.

After evacuation at 473 K the only band of contaminations remains at  $958 \text{ cm}^{-1}$  which is due to  $\text{Mo=O}$  groups, evidently, formed as a result of thiomolybdate hydrolysis during the precursor decomposition. The band is not sensitive towards CO or ammonia adsorption and should be assigned to  $\text{Mo}^{\text{IV}}=\text{O}$  groups with molybdenum ions coordinately saturated by sulfur in the form of  $\text{S}^{2-}$  and  $\text{S}_2^{2-}$  ions, or located in the bulk and not accessible for adsorption.

Most of the bands of contaminations that remain in the spectrum of the material after thiomolybdate decomposition at 423 K, but disappear after evacuation at 473 K, can be restored by ammonia adsorption and are similar to those observed earlier [1] for ammonia adsorbed on  $\text{MoS}_2$ . Isotopic splitting observed on adsorption of deuterated ammonia ensures us that the bands at  $1585$  and  $1215 \text{ cm}^{-1}$  of  $\text{NH}_3$  adsorbed on samples evacuated at 473 K are due to strongly held molecular ammonia, most probably, coordinated to Mo ions. In fact, the  $1215 \text{ cm}^{-1}$  band after addition of  $\text{ND}_3$  is split to four peaks, as should be expected for the  $\delta_s$  vibration of ammonia molecules.

The data on methanethiol adsorption reveal the existence of two forms of adsorbed species. Weakly held  $\text{CH}_3\text{SH}$  could be removed by pumping at room temperature, while chemisorbed methanethiol, that appears in small quantity at 300 K and is much more abundant after heating the sample in the adsorbate vapour at 393 K, resist pumping at 423 K, but can be removed by evacuation at 473 K. The bands of weakly adsorbed methanethiol are close to those of gas or liquid phase. In the spectrum of chemisorbed methanethiol, frequency shifts are greater (up to

about  $35\text{ cm}^{-1}$ ), and the band of C-S-H bending vibration is absent. This means that adsorption is dissociative, and we deal with the  $\text{CH}_3\text{S}$  groups, chemically bound to the surface.

Adsorption of  $\text{CO}_2$ ,  $\text{COS}$ ,  $\text{CS}_2$  and  $\text{SO}_2$  on sulfide samples pretreated at 423 K is completely reversible at ambient temperature, no bands of chemisorbed species were detected. Nevertheless, the bands of adsorbed molecules are shifted significantly, by up to  $25\text{-}45\text{ cm}^{-1}$ , with respect to those of gases. Within the limits of their coverage-dependant variations, the observed bands are at the same positions as reported in [1] for unsupported  $\text{MoS}_2$ . Unlike metal oxides,  $\text{CO}_2$  adsorption on the sulfide leads to  $\nu_{\text{as}}$  frequency lowering. The band of weakly bound CO is also shifted to lower wavenumbers. In both cases we believe that the side-on adsorption of molecules on the surface sulfur anions accounts for the the observed bands. CO band at  $2100\text{ cm}^{-1}$  is due to chemisorption with the backdonation from metal cations towards the adsorbate molecule. The band position for chemisorbed CO is sensitive to the state of sulfide and varies from  $2110\text{ cm}^{-1}$  for the supported  $\text{MoS}_2$  to  $2070\text{ cm}^{-1}$  for the air-contacted sintered material.

Thus, surface properties of the material obtained after *in situ* thiomolybdate decomposition at 423-473 K are very close to those of the earlier studied air-contacted crystalline  $\text{MoS}_2$  [1]. This reflects the structural resemblance of the material before and after sulfur elimination and crystallisation. In both cases, Mo is present in  $\text{Mo}^{\text{IV}}$  state. In the case of the *in situ* synthesis most of the cations are in a sulfided environment while only few cations are bound to some residual oxygen atoms forming  $\text{Mo}=\text{O}$  groups. Chemisorption of CO and ammonia reveal the presence of Lewis and Brønsted acidic surface sites. While evidence of methanethiol dissociation points out the existence of some acid-base pair sites on the  $\text{MoS}_2$  surface. Moreover, weak CO adsorption could occurs on the doubly or triply bridged sulfur atoms.

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