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FT-IR study of surface properties of unsupported MoS_2

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Abstract

Surface properties of unsupported MoS_2 have been studied by means of IR spectroscopy of a wide range of adsorbed molecules. After contact with air, surface of MoS_2 is partially oxidised and contains adsorbed water, Mo=O groups, sulphate and thiosulphate-like anions. These species are removable by treatment in vacuum or in H_2S–H_2 mixture. On MoS_2, only molecular adsorption was established for SO_2, CO_2, COS and CH_3SH showing weak basicity of surface sulphur ions. Unsupported MoS_2 presents also very weak acidic properties, as revealed by pyridine, 2,6-dimethylpyridine and ethylene adsorption. However, ammonia could be protonated or coordinately bound to MoS_2 surface. CO and NO interact with the coordinately unsaturated Mo sites of the sulphide, providing evidence for an important back donation effect. Comparison with surface properties of supported MoS_2 points to the lower acidic and higher metallic character of Mo sites of the unsupported sulphide. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Infrared spectroscopy; Surface sites; Unsupported MoS_2; Hydrotreating catalyst

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1. Introduction

Although oxide surfaces are rather well investigated, only few studies deal with the nature of adsorption on unsupported sulphides using IR technique, despite a great importance for catalysis, flotation, etc. This, evidently, is due to the difficulties of spectroscopic studies of sulphides because of their usually poor surface area, high scattering and strong light absorption.

In the earlier studies, effect of xanthate adsorption on Pb sulphide was studied using the KBr pellet technique [1]. Soon, the multiple reflection technique was applied to the same system in the form of evaporated films [2]. Nicholson [3] used the method of catalyst deposition on solid support from the slurry in isopropanol and water and further thermovacuum treatment. From the spectra of thiophene adsorbed on thus prepared MoS_2 and Co–MoS_2 systems, studied in the C–H stretching region, conclusions were drawn on the way of molecule–surface interaction via S, C or several atoms simultaneously.

Lubezky and Folman [4] succeeded to study CO adsorption at 77 K on ZnS films sublimated onto cooled support. Two forms of adsorption were detected, characterised by the bands at 2163–2171 and 2137 cm^{-1}. Although both are due to weak molecular adsorption, the former one corresponds to adsorption on “more energetic sites” because they could only be removed on evacuation at slightly higher temperature.

Two samples of ZnS powders with different crystalline structures and surface properties were studied by Hertl [5] using diffuse reflectance method. The

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author was able to characterise the material by the initially existing surface species, among which there were water, surface OH groups, sulphates indicating partial surface oxidation, and S–H groups. Using ammonia and pyridine as test molecules two kinds of surface Lewis sites were identified. Formation of $NH_4{}^+$ and pyridinium ions testified for the presence of Brønsted sites that were associated with surface OH groups.

Ratnasamy and Fripiat [6] have reported the S–H group formation after adsorption of hydrogen onto MoS_2-pressed samples and GeSx films. Two bands of these groups were detected at 2640 and 2500 cm^{-1} for the former, and only one at about 2575 cm^{-1} for the latter material. The multiplicity of S–H bands was explained by the existence of different valence states of Mo cations that besides Mo^{4+}, could be in Mo^{3+} or Mo^{2+} state.

Metal sulphides are mostly semiconductors and have the absorption edge in near-IR region. Above this edge, the light is strongly absorbed due to electron excitation. For PbS, the edge cuts the radiation at about 3500 cm^{-1} [2]. Absorption at lower wavenumbers is due to electron excitation within the conducting band or is due to impurities and could be strongly eliminated by the adsorption of electron acceptors, such as oxygen, that also leads to the gradual growth of new bands at 1130 and 985 cm^{-1} assigned to S–O stretching vibrations [2]. For MoS_2 absorption below the edge (about 10 000 cm^{-1}) was studied in [7] using photothermal deflection spectroscopy and was found to depend strongly on the crystal size, to be only slightly sensitive to oxygen adsorption and was associated with the presence of the edge planes of microcrystals. This absorption strongly eliminates the transparency of MoS_2 samples with high surface area, especially at high-frequency IR region. For this reason, several authors have tried other methods of vibrational spectroscopy to study the spectra of adsorbed molecules.

In a number of studies, strong light absorption of sulphides was overcome by using inelastic neutron scattering (INS) [8–16]. This technique enables optically opaque systems to be investigated and to detect both IR and Raman active modes [8]. The cross-section of scattering is the most important for the vibrations of light atoms, especially of hydrogen. Using INS technique, it was shown that, in the cases of tantalum and niobium sulphides, hydrogen atoms enter into the lattice and occupy positions in the plane of metal atoms surrounded by three metals [9]. The ability of MoS_2 to absorb hydrogen was found to depend on the method of preparation, however, the amount of hydrogen fixed by the solid was always much higher than to cover the surface accessible for nitrogen adsorption [10]. It was concluded that hydrogen is absorbed by the bulk, but the data of INS infer that unlike TaS_2 or NbS_2, it does not bind to metal atoms, but rather to sulphur atoms with the formation of S–H groups, that could not be detected by the used experimental technique for the unsupported sulphide. In the spectrum of MoS_2 supported on alumina, these authors have detected the band at 686 cm^{-1} that could be assigned to the bending mode of SH groups. In the study of amorphous MoS_2 [11], besides dissociative adsorption of hydrogen that leads to the S–H bending band at 662 cm^{-1} and is saturated at less than 1 atm of H_2 at temperatures below 423 K, a second type of hydrogen adsorption was found that needs higher pressures and occurs much more effective at temperatures above 423 K.

Jones et al. [12] have also observed the formation of S–H groups with the band at 662 cm^{-1} (82 meV) as a result of hydrogen dissociation on MoS_2, and have shown that the second form of adsorbed hydrogen is molecular adsorption, although it needs activation. It leads to the forbidden in optical spectra *para–ortho* rotational transition at 121 cm^{-1} (15 meV), slightly higher than for the pure hydrogen (14.7 meV).

Tungsten disulphide forms the same type of layered structure as MoS_2. Hydrogen adsorption on it was studied by INS [13], and was found to be also activated. It leads at 673 K to strong band at 694 cm^{-1}, accompanied by weaker overtone maxima at 1380 and 2074 cm^{-1}, as well as by two more features at 2470 and 2679 cm^{-1}. These latter were reasonably attributed by the authors to the stretching modes of two kinds of S–H groups, similar to those observed in the IR spectra of MoS_2 in [6].

Hydrogen adsorption was also studied by INS spectroscopy on RuS_2 surface. This sulphide has three-dimensional pyrite-type structure containing $S_2{}^{2-}$ anions. Preliminary temperature-programmed desorption data [17] exhibit at least two different hydrogen species that remain adsorbed after evacuation at 300 K, the concentrations of which depend on the degree of reduction of the sample. ^1H NMR studies of the reduced RuS_2 samples revealed two signals ascribed to S–H groups and to hydride-type adsorbed species [18]. In accordance with these results, in the INS spectra two species were identified. A couple of bands at 600 and 710 cm^{-1} [14], or at 646 and 719 cm^{-1} [15] were assigned to two non-degenerate S–H bending modes [15], while two more bands at 540 and 823 cm^{-1} were attributed to the bending vibrations of two kinds of Ru–H species [15].

Recently, the INS spectroscopy was used to study ammonia adsorption on RuS_2 [16]. Adsorption was found to be rather weak on unreduced sample, while after partial desulphurisation, dissociative adsorption occurs. The latter leads to the formation of SH groups (band at 680 cm^{-1}) and NH_2 groups bound to unsaturated ruthenium ions, identified by a complex band centred at 100 cm^{-1} due to hindered translation and rotation modes.

It could be concluded that the advantages of IR technique for studies of sulphide surfaces has not been used enough. The materials are rather transparent in the low-frequency region that for oxides is almost completely closed by a very strong bulk absorption. Spectra of bending vibrations of surface functional groups such as SH or OH that occur in this region contain important information about local arrangement and are not less sensitive to the adsorption than the OH stretching mode, well explored in routine studies of oxide catalysts. However, with only few exceptions (e.g. [5]), no works deal with weak adsorption of simple test molecules on unsupported sulphides, particularly at low temperatures.

Thus, the aim of this work was to study by means of IR spectroscopy in sufficiently wide spectral region, down to 500 cm^{-1}, the surface properties of unsupported MoS_2 phase, their changes on sample treating in different conditions and adsorption of some molecules at 77–300 K that could be helpful as tests for the presence of certain surface sites. As a first object, the powders of MoS_2 were used in the form of pressed pellets, treated in vacuo or sulphided in the $H_2 + H_2S$ mixture. A wide range of adsorbed molecules with different properties were tried as tests, such as water, O_2, ozone, hydrogen, H_2S, SO_2, CH_3SH, ethylene, ammonia, pyridine, lutidine (2,6-dimethylpyridine, DMP), CO and NO.

2. Experimental

The earlier described [19] 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 us to register the spectra up to about 600 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 was attached directly to the sample-containing compartment of the cell. Another one enabled us to measure a dose of gas in the known volume before letting it into the cell. The sample temperature during the treatment or registration of spectra was monitored by a chromel–alumel thermocouple inserted into the heater or into the coolant compartment of the cell. For spectra registration at very low temperature, 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 cooling agent, the temperature of the sample did not differ from 77 K more than by 5 K.

MoS_2 was prepared by decomposition of ammonium tetrathiomolybdate by heating from 300 to 673 K and treating for 4 h at 673 K under $H_2S(15\%)$–H_2 flow with further cooling up to 330 K in this sulphiding mixture and was kept under dry argon. The so-prepared sample presents a specific area of 56 $m^2\,g^{-1}$ and observations by electron microscopy indicate that it is constituted of small particles presenting a mean length of 4.5 nm with a stacking close to four slabs [20].

Batches of about 20 mg of MoS_2 were taken out of argon and pressed in the air into 2 cm^2 self-supporting pellets. The latter were treated in vacuum at different temperatures to see first the bands of originally present contaminations. Then, adsorption on this partially oxidised surface was studied. We call below such air-contacted MoS_2 catalyst outgassed at 673 K as “evacuated” MoS_2. Alternatively, “sulphided” samples were prepared by treatment in 80 Torr of $H_2S(15\%) + H_2$ mixture at 673 K. Three cycles of such treatment for 30 min with 10 min of evacuation between them followed by final pumping at the same temperature were sufficient to remove the bands of oxygen-containing species and to have a clean background spectrum. However, the transparency of these sulphided pellets was lower and some results could only be obtained with evacuated samples.

Commercial pyridine, lutidine, H_2S, H_2 and O_2 were used. Ozone was prepared from gaseous O_2 by electric discharge and manipulated as earlier [21]. Spectra of adsorbed CH_3SH, pyridine and lutidine were studied at 300 K. Spectra of H_2, O_2, CO, NO, O_3, CO_2, H_2S and NH_3 were normally registered at 77 K. While the five former gases could be adsorbed already at 77 K, for the four others and to some extent for ozone as well, the vapour pressure at nitrogen temperature is not sufficient for adsorption. To observe these species in the adsorbed state, after their introducing, the 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 registered with a Nicolet Magna 550 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 in the 4000–650 cm^{-1} region. For the 650–600 cm^{-1} region, a DTGS detector was used. The spectrometer operated at 4 cm^{-1} resolution collecting 512 scans.

3. Results

3.1. Characterisation of the air-contacted material, influence of treatment in H_2 and H_2S

The evolution of the spectrum of an air-contacted non-supported MoS_2 pellet after different pre-treatment procedures is illustrated in Figs. 1 and 2. The material is rather transparent below 1000 cm^{-1}, however, as seen from Fig. 1, the absorbance gradually grows with the frequency. For our pressed pellets it reaches 3.5–4 at about 2500–3000 cm^{-1} and registration of the bands of surface species at higher wavenumbers is no more possible. The initial spectrum of MoS_2 exhibits a band at 1630 cm^{-1} with a broad shoulder on the high-frequency side that has a poorly resolved maximum at about 1700 cm^{-1} and stretches up to 1900 cm^{-1}. Several strong bands occur below 1400 cm^{-1}. Most of these bands disappear after thermo-evacuation at 673 K (curve 2) when the

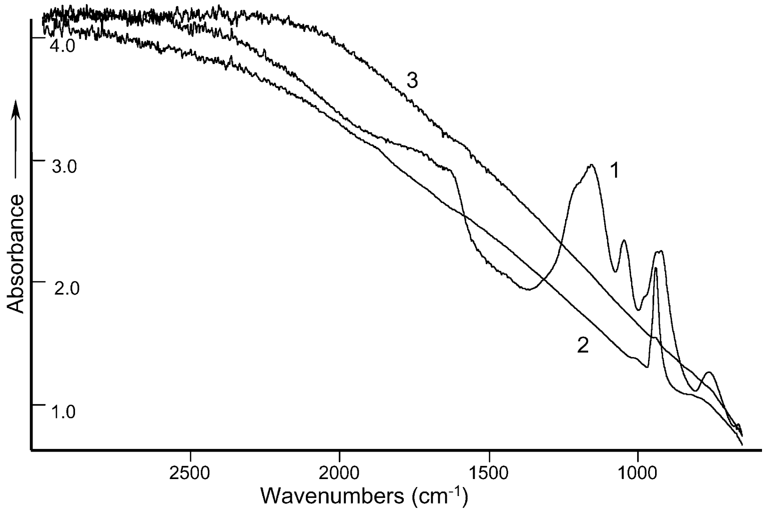


Fig. 1. IR spectrum of the air-contacted MoS_2 pellet (1), after evacuation at 673 K (2) and after treating in H_2–H_2S mixture at 673 K (3).

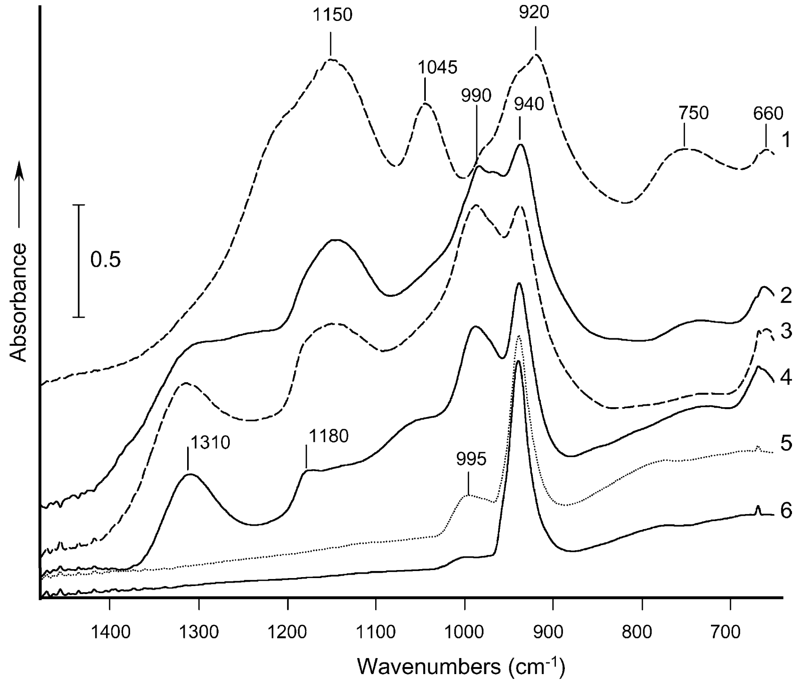


Fig. 2. IR spectrum of the air-contacted MoS_2 pellet (1), after evacuation at 300 K (2), 373 K (3), 473 K (4), 573 K (5) and 673 K (6). Absorption of the sample treated in H_2–H_2S mixture at 673 K (curve 3, Fig. 1) is subtracted.

overall absorbance somewhat increases. Spectrum of sulphided sample (curve 3) is almost free from any absorption bands, but is even less transparent, practically opaque above 2000 cm^{-1}.

Fig. 2 shows the development of absorption below 1400 cm^{-1} with the increasing temperature of evacuation. In the initial spectrum strong bands could be observed at 1150 cm^{-1} (with a shoulder at 1220 cm^{-1}), at 1045, 920 cm^{-1} (with a shoulder at 940 cm^{-1}), 750 and at about 660 cm^{-1}. Evacuation at room temperature results in the disappearance of the bands at 1045 and 750 cm^{-1} together with dramatic diminution of absorption at 1630–1700 cm^{-1}. The massif at 1150–1220 cm^{-1} becomes split into two bands at 1310 and 1180–1150 cm^{-1}, while the intensity of 940 cm^{-1} band increases at the expense of maximum at 920 cm^{-1}. Meanwhile, the 670 cm^{-1} peak also becomes more pronounced and a feature presented as a shoulder on spectrum 1 develops at about 990 cm^{-1}. The bands at 1310 and 990 cm^{-1} continue to grow after vacuum treatment at 373 K when the 660 cm^{-1} band reaches its maximum intensity and most of other bands continue to diminish. After 473 K, the bands at 1650–1750, 920 and 1150 cm^{-1} disappear completely. Raising the temperature up to 573 K leaves only the band at 940 cm^{-1} with a weaker maximum aside at 995 cm^{-1}. After evacuation at 673 K, the 940 cm^{-1} band with a weak shoulder at 960 cm^{-1} (observed on spectrum 1 of Fig. 3) and at 995 cm^{-1} is the only one to remain.

The band at 940 cm^{-1} is very sensitive to the adsorbed species. The most prominent effect was observed in presence of water or NH_3, as illustrated in curves 3 and 4 of Fig. 3. In the presence of large quantity of weakly adsorbed D_2O molecules, the complete disappearance of the band is observed, instead of which a maximum at 928 cm^{-1} appears. Pumping at 300 K results in the shift of the maximum to higher wavenumbers, but the band is only restored when molecular D_2O is eliminated by evacuation at high temperature. Similar reversible changes were previously described in Fig. 2 when the removal of adsorbed water by pumping at 300–373 K caused the growth of 940 cm^{-1} band at the expense of that at 920 cm^{-1}.

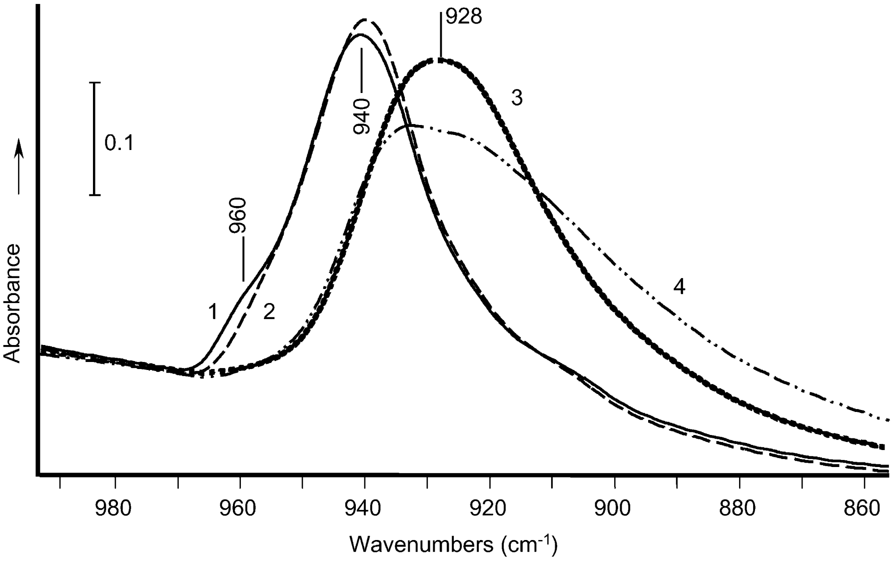


Fig. 3. Changes of IR spectrum of the evacuated MoS_2 sample (1), after adsorption of CO (9 Torr) at 77 K (2), D_2O (13 Torr) at 300 K (3) or ammonia (3 Torr) at 250 K (4).

Ammonia adsorption causes the same effects on the 940 cm^{-1} band. Evacuation at 323 K restores the original spectrum, despite the presence of the bands due to strongly held ammonia. Similar, but less pronounced reversible changes were observed in the case of weakly adsorbed molecules. Thus, CO adsorption only results in disappearance of the high-frequency shoulder at 960 cm^{-1} and in growing intensity on the low-frequency side of the band (Fig. 3, curve 2).

Treating the sample in the $H_2S(15\%) + H_2$ mixture at 673 K removes these bands and results in a drastic decrease of the sample transparency. Besides sulphidation, we have studied separately the influence of treatment in H_2 and H_2S at progressively increasing temperatures on the spectrum of evacuated MoS_2 sample (spectra not shown here). Adsorption of hydrogen alone at 77 K causes intensity diminution of the 960 cm^{-1} shoulder and increased intensity at the low-frequency side of the 940 cm^{-1} band. Heating in H_2 up to 423 K leads to the decrease of 940 cm^{-1} band intensity and to disappearance of residual absorption at 780–730 cm^{-1}. The band at 995 cm^{-1}, that was not completely removed by pre-treatment, shifts meanwhile to higher wavenumbers, up to 1010 cm^{-1}. Further raising the temperature up to 573–673 K in the presence of even 760 Torr of H_2 increases the overall absorption and results in strong intensity elimination of the bands at 940 and 780–730 cm^{-1} but does not lead to the appearance of any new bands. The maximum at 1010 cm^{-1} turns to be the most resistant to the treatment in H_2 and was seriously reduced only after heating at 673 K.

Adsorption of H_2S at 120 K on the evacuated pellet (spectrum not shown) results in very weak maxima at 2560 and 1167 cm^{-1} as well as in the band at about 2035 cm^{-1} of admixed COS, which is present as impurity in H_2S, and is shown in Fig. 5. In the presence of H_2S, strong diminution of all the 1010, 940 and 730 cm^{-1} bands occurs already at 300 K, and after heating at 473 K only a trace of absorption remains at about 930 cm^{-1}.

3.2. Adsorption of ozone, SO_2, COS, CO_2 and CH_3SH

To find out, to what extent sample reduction in the H_2–H_2S mixture is reversible, we have studied adsorption of oxygen and ozone at the surface of sulphided sample. Addition of 6 Torr of O_2 at 77 K does not lead to any noticeable changes in the spectrum. Ozone adsorption at 77 K (Fig. 4) results in a strong band at 1028 cm^{-1} and less intense at 1102 and 702 cm^{-1}

that are very close to the ν_3, ν_1 and ν_2 modes of free O_3 molecule and are, evidently, due to physisorbed ozone. These bands first increase when the temperature is raised by several K, then decrease and disappear on heating up to about 140 K. Simultaneously, already at 77 K, bands at 1321, 1144 and 940 cm^{-1} arise and start to grow, two more peaks show up at 1180 and 1050 cm^{-1}.

The assignment of the bands initially present in the spectra of the evacuated MoS_2 sample (Fig. 2), evidently connected with sulphide surface oxidation, could be clarified by comparison with the spectra of adsorbed sulphur and oxygen-containing molecules. When SO_2 is added at about 120 K, it gives rise to the bands at 1327 and 1141 cm^{-1} (curve 4 in Fig. 4), almost coinciding with the two bands observed after O_3 adsorption. These bands diminish on raising the temperature, slightly changing their position with coverage, and can easily be removed by pumping at 200 K or lower.

Spectra of adsorbed COS and CO_2 at 77–110 K on evacuated MoS_2 are illustrated in Fig. 5. In both cases, the positions of the observed bands are close enough to those of free molecules in gas phase (2062 and 859 cm^{-1} for COS and 2349 cm^{-1} for CO_2 [22]), slightly shifted towards lower wavenumbers. As seen from Fig. 5, coverage lowering results in additional downward shifts of these bands, from 2331 to 2326 cm^{-1} for CO_2 and from 2038 to 2032 cm^{-1} for COS. One more narrow band of C–S vibration of adsorbed COS was detected at 857 cm^{-1}. No other bands were observed, besides those due to molecular adsorption.

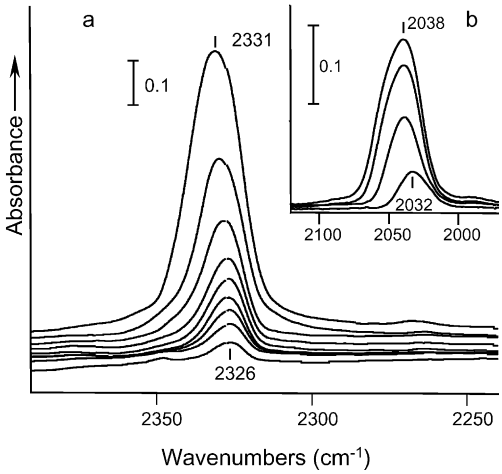


Fig. 5. IR spectra of CO_2 (a) and COS (b) adsorbed at different coverages on evacuated MoS_2, recorded at 77–110 K. Spectrum of the sample before adsorption is subtracted.

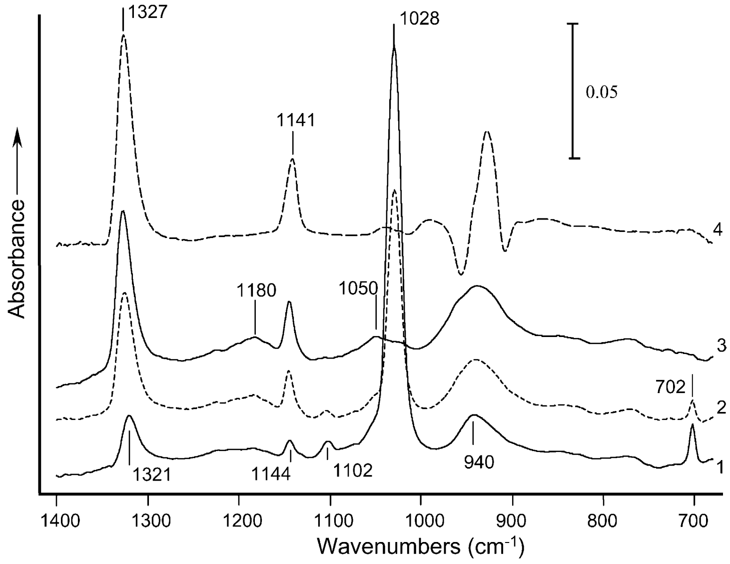


Fig. 4. IR spectrum of sulphided MoS_2 after adsorption of ozone at 77 K (1), 20 min later (2) and after raising the temperature up to 110 K (3). Spectrum of evacuated MoS_2 after adsorption of SO_2 and cooling up to 77 K (4). Spectrum of sample before adsorption is subtracted.

Adsorption of CH_3SH at room temperature on evacuated MoS_2 (spectrum not presented here) results in the bands at 1414, 1298, 954 and 780 cm^{-1}. These bands decrease in intensity on evacuation at 300 K and could be removed by pumping at elevated temperature.

3.3. Adsorption of electron-donating test molecules

Fig. 6 shows the infrared spectrum of sulphided MoS_2 after adsorption of molecules that are often used as tests for surface acid sites of oxide adsorbents. NH_3 adsorption at 160 K on the sample sulphided at 673 K in H_2–H_2S mixture (curve 1) results in the bands at 1619 cm^{-1} with a shoulder at 1590 cm^{-1}, and at 1490, 1250 and 1080 cm^{-1}. Evacuation at 300 K diminishes dramatically their intensities, while the maximum of the latter shifts gradually to 1125 cm^{-1}. After pumping off at 423 K most of these bands disappear completely, but the group of bands at 1590, 1245 and 940 cm^{-1} still remains in the spectrum, and cannot be removed completely even at 523 K. The same groups of bands could be observed after NH_3 adsorption on the evacuated sample, however the band in the 1490–1450 cm^{-1} region is less intense. This band could be naturally associated with the formation of NH_4^+ ions, and to find the source of Brønsted acidity, effect of H_2S and water adsorption on the intensities of the bands of adsorbed ammonia has been studied. H_2S adsorption at 300 K does not affect noticeably the spectrum of NH_3, however after preliminary H_2O addition, the absorption at 1490–1430 cm^{-1} is enhanced.

Curve 2 in Fig. 6 shows the IR spectrum of ethylene adsorbed at 100 K on the sulphided sample. The intense band of ν_7 vibration of C_2H_4 is known to move to higher wavenumbers on interaction with Lewis sites or H-bonding [23]. In our case, the band of this mode arises at 949 cm^{-1}, exactly as for the free molecule in the gas phase. One more ethylene band appears at 1434 cm^{-1}. Evacuation at about 100 K removes all the adsorbed C_2H_4 species.

Adsorption of pyridine at 300 K on sulphided sample is illustrated by curve 3 in Fig. 6. The bands, the most intense being observed at 1597, 1581, 1482, 1437, 748 and 705 cm^{-1}, could be removed completely by prolonged evacuation at 300 K. As far as their positions practically coincide with those known for liquid pyridine, most of these bands should be attributed to physisorbed species. The only band somewhat shifted due to adsorption is that at 1597 cm^{-1}.

DMP adsorption at 300 K (Fig. 6, curve 4) on the sulphided sample results in bands, in particular, at 1593, 1580, 1468, 1453 and 772 cm^{-1}. As in the case of pyridine, all the bands disappear after evacuation at 300 K and should be assigned to physisorbed molecules. No other bands that could be due to protonated form or coordinated molecules were detected.

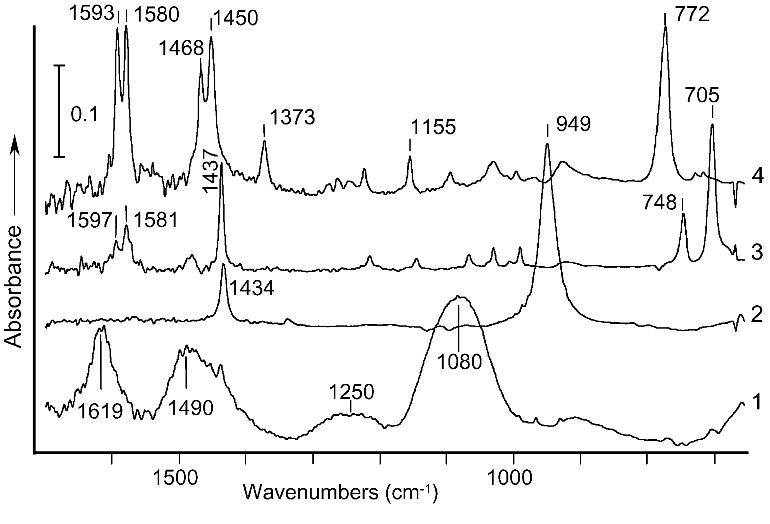


Fig. 6. IR spectrum of sulphided MoS_2 after adsorption of NH_3 (1 Torr) at 160 K (1), ethylene (10 Torr) at 130 K (2), pyridine (4 Torr) at 300 K (3), and 2,6-dimethylpyridine (4 Torr) at 300 K (4). Spectrum of the sample before adsorption is subtracted.

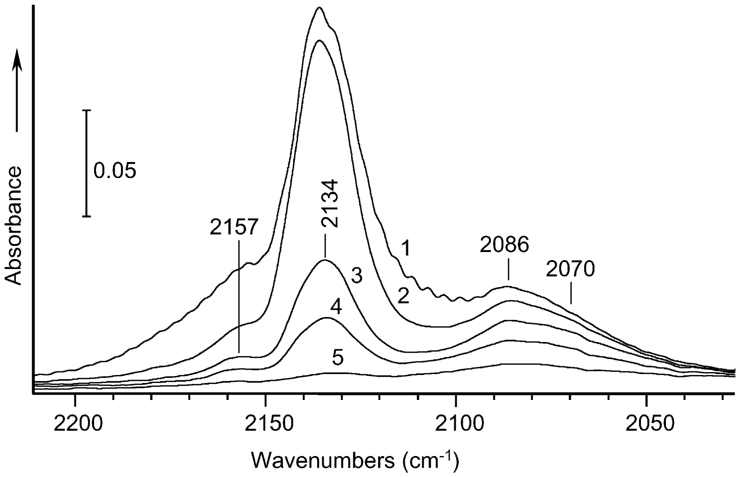


Fig. 7. IR spectrum of evacuated MoS_2 after adsorption of CO (9 Torr) at 77 K (1), and after subsequent evacuation at about 100 K for 5 s (2), 15 s (3), 30 s (4) and 60 s (5). Spectrum of the sample before adsorption is subtracted.

3.4. Low-temperature adsorption of CO and NO

Low-temperature adsorption of CO at 77 K on evacuated MoS_2 sample is illustrated in Fig. 7. A band at 2134 cm^{-1} with a shoulder at 2157 cm^{-1} was observed in the presence of 9 Torr of CO. Another broad band with a maximum at 2086 cm^{-1} and a shoulder at 2070 cm^{-1} becomes more intense if the sample is heated in the presence of CO up to 300 K and cooled again to 77 K. All these bands considerably decrease in intensity after prolonged evacuation at about 100 K, the rate of decrease being higher for the 2134 and 2157 cm^{-1} bands. Evacuation at 300 K removes all the traces of adsorbed CO.

Spectrum of CO adsorbed on sulphided MoS_2 catalyst has very low signal-to-noise ratio because, as could be seen from Fig. 1 (curve 3), the sample absorption above 2000 cm^{-1} is very high. Nevertheless, a sharp band at 2134 cm^{-1} and a broad maximum at about 2070 cm^{-1} could still be distinguished. Position of the 2134 cm^{-1} band enables us to assign it to physysorbed CO. The shoulder at 2157 cm^{-1}, observed in the spectrum of the evacuated sample, is likely to be due to CO interacting with the Mo–OH groups formed when the sample was in contact with the humid air. The assignment of these two bands is in agreement with their low stability towards evacuation. The low wavenumber massif observed both for the evacuated and sulphided pellets corresponds to CO bound to the Mo sites. The frequencies of CO molecules are lowered due to the back donation of d-electrons of molybdenum to the antibonding orbitals of CO, like in metal carbonyls.

NO addition at 77 K to the evacuated pellet (Fig. 8) immediately leads to a couple of bands at 1855 cm^{-1} and a more intense one at 1756 cm^{-1} that disappear after pumping off at about 120 K. When after NO adsorption at 77 K, the sample temperature is raised up to about 300 K and lowered again to 77 K, another couple of less intense and broader bands at 1775 and

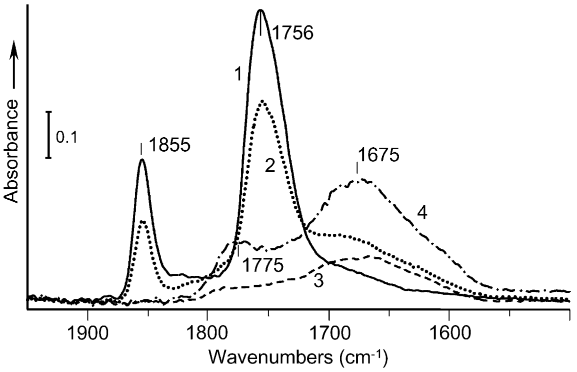


Fig. 8. IR spectrum of evacuated MoS_2 after adsorption of NO at 77 K (1), after raising the temperature up to 300 K for 5 min and cooling at 77 K (2), evacuation at about 120 K for 45 min (3), and in the presence of NO (60 Torr) at 300 K (4). Spectrum of the sample before adsorption is subtracted.

1675 cm^{-1} show up. They become even more intense if the spectrum of adsorbed NO is ran at 300 K. On evacuation at 300 K gradual decrease of their intensities occurs, however, even after 30 min these bands still remain in the spectrum.

NO adsorption at 77 K on the sulphided sample (spectrum not presented here) also results first in a couple of easy removable bands with maxima at slightly higher wavenumbers, at 1858 and 1759 cm^{-1}. The band at 1755 cm^{-1} arises as well after raising the temperature in the presence of NO. If the spectrum is registered at 300 K, instead of one broad band at lower wavenumbers, as observed on the evacuated sample, two separate maxima could be observed at about 1690 and 1610 cm^{-1}.

4. Discussion

4.1. Surface species of the air-contacted MoS_2

The high absorbance of the studied dispersed MoS_2 samples that decreases with the frequency lowering is in agreement with earlier results [7]. Slight absorption increase after vacuum treatment at elevated temperatures and much more serious transparency loss after treatment in the H_2S–H_2 mixture could be due to the reduction of the material in these conditions. The fact that initial transparency of pellets is not recovered after O_2 and even O_3 adsorption shows that the reduction is not easily reversible and is in accordance with the data on low sensitivity of IR absorption of MoS_2 to oxygen [7].

Among the impurities detected in the MoS_2 sample that was contacted with atmosphere, weakly adsorbed water should be mentioned (band of the bending vibration at 1630 cm^{-1}). The broad high-frequency tailing of this band could be due to the hydronium H_3O^+ ion that in different compounds has the band of ν_4 mode in comparatively wide 1700–1577 cm^{-1} region [22] although presence of strong Brønsted acid sites on MoS_2 is not revealed by basic probe molecule adsorption. The symmetric bending vibration ν_2 of H_3O^+, which for the condensed systems varies between 1175 and 1095 cm^{-1} [22], could account for absorption maxima of surface species at 1220 and 1045 cm^{-1} that like the band at 1630 cm^{-1} disappear on evacuation at 300 K. Absorption at 750 cm^{-1} could be due to the liberation mode of molecular water.

In the complex spectrum of the 1310–990 cm^{-1} region bands at 1310, 1180, 1050, 990, and at 660 cm^{-1} whose intensity increases after water elimination are apparently due to sulphate species presenting a low-covalent character [24]. The highest wavenumber band corresponds to S=O vibration while the others should be due to the stretching and bending modes of the S–O bonds. The part of the massifs at ~1180 and 660 cm^{-1} could also be attributed to the thiosulphate ion $S_2O_3{}^{2-}$. In fact, this ion, besides absorption maxima at about 1123 and 995 cm^{-1}, has a band at 669 cm^{-1} [24], very close to the observed one. Such species do not arise after SO_2 adsorption at 300 K, but it is noteworthy that when the surface is oxidised by ozone, among others, the bands at 1180 and 1050 cm^{-1} appear that are close to some of bands initially present in the spectrum of the evacuated air-contacted MoS_2 sample.

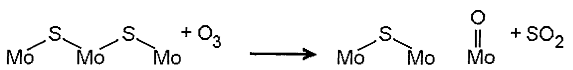
Note that, in previous studies, bands around 680 cm^{-1} were attributed to the S–H groups arising as a result of dissociative H_2 adsorption on MoS_2 [10–12]. In our case, however, the 660 cm^{-1} band disappears after evacuation at 573 K together with most of the bands in the 1310–1000 cm^{-1} region, and subsequent adsorption of hydrogen or H_2S (or treatment in these gases at elevated temperatures) does not restore it. Thus, the 660 cm^{-1} band, observed in this work, is rather characteristic of bending vibration of S_xO_y species.

The bands at 940 and 1010–995 cm^{-1} have the position typical of terminal metal-oxygen double bonded groups. Indeed, the band of Mo=O groups of the amorphous MoO_3 films was observed at 990 cm^{-1} [25]. In the case of molybdate phase supported on zirconia or titania, the Mo=O band was found at 991 cm^{-1} and was shown to produce one band at 950 cm^{-1} after ^{18}O substitution, indicating the presence of only one Mo=O bond [26]. The above results infer that such groups are available for adsorbed molecules, since all the bands at 1010–940 cm^{-1} could be perturbed by water, ammonia or H_2S. Similar reversible perturbation of the metal-oxygen double bond by adsorption of H_2O, NH_3 has already been reported for tungstate species supported on alumina [27]. These changes were related to the adsorption of the bases on the tungsten atom that was supposed to be coordinately unsaturated.

The molybdate species that account for 940 and 995 cm^{-1} bands could be removed by treatment in hydrogen, H_2S or their mixture, but reveal different reactivity towards H_2 and H_2S. Molybdate groups that absorb at 995 cm^{-1} are more sensitive to sulphidation by H_2S, that occurs already at 300 K, and are more resistant to heating in H_2, while the species that account for the 940 cm^{-1} band can easier be reduced by hydrogen treatment, but are more stable towards H_2S. Moreover, selective perturbation of the high-frequency side of the 940 cm^{-1} band (shoulder at 960 cm^{-1}) on CO and H_2 adsorption point to heterogeneity of these Mo=O groups.

The band at 1010–990 cm^{-1}, with the frequency equal to that of Mo=O groups in MoO_3 films, can be attributed to metal-oxygen vibrations of the groups where molybdenum is in a higher oxidation state (Mo(VI)) and is linked only to oxygen atoms. Such molybdenum oxide-like phase or clusters can easily be destroyed by sulphidation in H_2S. The 940 cm^{-1} band should be characteristic of oxysulfide species, where the Mo=O group is bound to the bulk via sulphur atoms. Different coordination of molybdenum atom by sulphur could account for the difference between 940 cm^{-1} band and the shoulder at 960 cm^{-1}.

Ozone addition at 77 K, besides weak molecular adsorption with the frequencies close to those of gas or of O_3 physisorbed on oxides [21], results in the bands of adsorbed SO_2 (1321 and 1144 cm^{-1}) as well as to the band of Mo=O groups at 940 cm^{-1}. Apparently, the following reaction occurs:



Subsequent ozone interaction with SO_2 could lead to SO_3 formation. Reaction of the latter with S^{2-} should result in the formation of thiosulphate ions that account for weak bands at 1180 and 1050 cm^{-1}. Therefore, analysis of the surface of the air-contacted sample points to its heterogeneity, since besides the presence of regular MoS_2, several different oxidation products could be detected.

4.2. Acid–base properties of the evacuated and sulphided MoS_2

By analogy with metal oxides, where “associative” adsorption of CO_2 and SO_2 leads to surface carbonates and sulphites, one could anticipate that on sulphides these molecules will interact with surface S^{2-} ions with the formation of thiocarbonates CO_2S^{2-} and thiosulphites $S_2O_2{}^{2-}$. However, it does not occur, and on MoS_2 surface CO_2, COS, and SO_2 do not display anything else, but weak molecular adsorption at low temperatures. In their earlier work, Ramis et al. [28] reported that on metal oxides low-temperature CO_2 adsorption results rather in linearly coordinated CO_2, but not to carbonate or bicarbonate species. However, on ZrO_2, TiO_2 and Al_2O_3, some carbonate species are formed already at low temperature. Thus, our results are scarcely influenced by the conditions of experiment, but point to weak basicity of surface sulphur ions of MoS_2.

In the same way, since dissociative adsorption of alcohols on acid–base pair sites of oxides leads to the formation of hydroxyl and alkoxyl groups, it could be expected that CH_3SH would dissociate on sulphides. And again, as far as only molecular adsorption of CH_3-SH was detected, we can state that the corresponding pair sites on sulphide surface are not strong enough.

For oxides, molecular adsorption of carbon dioxide occurs on Lewis acid sites and results in the increase of ν_3 frequency with respect to that of gaseous CO_2 [29]. Here, on the contrary, the bands of CO_2 and COS are shifted to lower wavenumbers by 24 and 18 cm^{-1}, respectively. Hence, molecular adsorption of these gases occurs on MoS_2 not in the same way, apparently because of the absence of Lewis sites of sufficient strength. Frequency lowering takes place also for the ν_3 mode of SO_2 adsorbed on MoS_2, 1327–1321 cm^{-1} against 1351 cm^{-1} for the gas phase [22], but this is typical of SO_2 adsorbed on oxides with different properties [30,31], such as for weak adsorption on silica (1343 cm^{-1}), chemisorption on acid sites of Al_2O_3 (1326 cm^{-1}) or basic oxygen centres of MgO (1320 cm^{-1}).

Ammonia and pyridine are classic test molecules for Lewis and Brønsted acid sites [32]. DMP is an excellent test for Brønsted acidity [33–35], and ν_7 band of ethylene is also sensitive for Lewis acidity and H-bond strength. However, only physical adsorption of ethylene and DMP was observed on MoS_2 revealing the absence of any measurable Lewis or Brønsted acidity. Small increase of ν_{8a} frequency of pyridine up to 1597 cm^{-1} infers that Lewis acidity of MoS_2 surface is very low.

Bands at 1080–1125 cm^{-1} which arise after ammonia adsorption at 160 K is typical of δ_{sym} vibration of H-bonded molecules on oxide surfaces [32] and is only slightly higher than in solid NH_3 (1060 cm^{-1} [22]). On sulphide, H-bond could be formed by N–H groups of ammonia with surface S^{2-} ions or with N atoms of adjacent ammonia molecules. Bands at 1619 cm^{-1} is characteristic of coordination while bands at 1590, 1250 and 970 cm^{-1} are characteristic of δ_{as}, δ_{sym} and ρ_r vibrations of amino complexes [22] or of NH_3 molecules coordinated to rather strong surface Lewis acid sites, such as those of Al_2O_3 or ZrO_2 and stronger than those of TiO_2 or ZnO [32]. Such a strong chemisorption of ammonia was unexpected for the surface where pyridine and DMP adsorption reveal the absence of any strong Lewis acidity.

The most interesting feature, observed on ammonia adsorption, is the appearance of a band at 1490 cm^{-1}, which should be attributed to ammonium NH_4^+ ions. It can be surprising since no Brønsted acidity is detectable by DMP or pyridine. To explain this result, at least, two hypotheses should be considered.

1. Protonation is caused by ammonia dissociation into a NH_2^- group and a proton, that becomes a source of Brønsted acidity. Such effect was recently observed for oxides, when dissociative adsorption of H_2S led to the increased number of Brønsted sites, that were identified as surface OH groups [36]. However, no other bands, that could be assigned to NH_2^- species, were observed, besides those at 1590, 1250 and 970 cm^{-1}, and their positions are somewhat different from the values known for surface or bulk NH_2 groups, that normally have their δ vibration in the 1570–1520 cm^{-1} region [22,32], while ρ_w and ρ_r modes lie lower than the observed frequencies.
2. Protonation of NH_3 occurs on Brønsted acid sites, which exist on MoS_2 surface, but are not strong enough to protonate other probe molecules with lower basicity than ammonia. In fact, for ammonium, lutidinium and pyridinium ions, pK_a values are equal to 9.24, 6.15 and 5.25, respectively. Therefore, formation of ammonium ions should be favourable on unsupported MoS_2 with certain amount of SH groups of moderate acidity.

Information about surface site properties could also be drawn from the spectra of adsorbed CO. Position of the 2134 cm^{-1} band enables us to assign it to physisorbed CO. The shoulder at 2157 cm^{-1}, observed on the evacuated sample, could be attributed to CO adsorbed on the OH groups bound to Mo ions of oxidised surface. It should be mentioned that CO adsorption on surface OH groups of pure MoO_3 results in a more important frequency increase, up to 2163 cm^{-1} [25]. The most interesting are the bands in the 2086–2070 cm^{-1} region, which belong to the most stable surface CO species and are due to molecules adsorbed on Mo sites. These Mo cations have, evidently, a sulphided environment, as soon as these bands were observed for both evacuated and sulphided pellets, although for the latter the maximum was detected at lower wavenumbers indicating stronger back donation of d-electrons of molybdenum to the antibonding orbitals of CO.

The data on NO adsorption are in coherence with CO results. The couple of bands at 1855 and 1756 cm^{-1} is due to NO dimers weakly bound to the surface. Another pair of broader bands at 1775 and 1675 cm^{-1} corresponds to $(NO)_2$ species coordinated to surface Mo cations [37,38]. On evacuated MoS_2, the band maxima are slightly shifted towards lower values with respect to wavenumbers previously reported for dinitrosyl species adsorbed MoS_2 supported on alumina [37]. On the sulphided MoS_2 catalyst, NO adsorption gives rise to the bands at even lower positions, that like in the case of CO infers stronger back donation.

4.3. Comparison with the supported MoS_2

Comparison of the surface properties of unsupported MoS_2 with the results previously obtained for the supported MoS_2 catalyst is tempting. However, strongly different morphology of the two MoS_2 phases could lead to catalysts presenting very different number of sites, that could impede any comparison. So, as a first step, taking into account the microscopy data and specific area previously measured with the hypotheses that all the particles have hexagonal shape and that adsorption sites are located on the $(1\,0\,\bar{1}\,0)$ and $(\bar{1}\,0\,1\,0)$ planes, we have evaluated the number of surface sites of the unsupported pellet. Since this calculation leads to the value of about 300 $\mu mol\,g^{-1}$, that is almost equal to the value reported for alumina-supported catalyst containing 10% Mo [39], such a comparison could be performed.

This comparison shows that, when supported, MoS_2 develops higher acidic properties than unsupported phase. Indeed, Brønsted acid sites of the MoS_2 phase were able to protonate lutidine when supported on alumina [34,35]. In the same way, supported MoS_2 presents slightly stronger Lewis acid sites since pyridine gives rise to a ν_{8a} band at $1602\,cm^{-1}$ while on bulk pellet only physisorbed species are detected [40].

Comparison of bands due to CO adsorption also provides evidence for some differences. On the supported catalyst, CO adsorption gives rise to a main band at $2110\,cm^{-1}$ with a weak shoulder at about $2070\,cm^{-1}$ [41–45]. The presence of two ν(CO) bands was associated with dissimilarity of surface Mo^{4+} ions, that could have different coordination because of their location in unequivalent positions, either on edge or corners, or on different crystallographic faces [43,44]. In the case of unsupported MoS_2, any absorption near $2110\,cm^{-1}$ is absent, while the low-frequency component predominates. It consists of two constituents with maxima at 2086 and about $2070\,cm^{-1}$, the latter being the more intense after sulphidation. These results reveal more metallic character of Mo sites with respect to those of the supported catalyst. The absence of the $2110\,cm^{-1}$ band could also be explained by a specific poisoning of Mo sites. Indeed, it has been reported that contact of the sulphided MoS_2/Al_2O_3 with air leads to its irreversible modification, and initial surface properties could not be recovered even by re-sulphidation [44,45]. Unsupported MoS_2, prepared by thiomolybdate decomposition, was air-contacted before pelletising, and we could not exclude that the absence of band at $2110\,cm^{-1}$ could be due to the site poisoning during the contact with atmosphere. Decomposition of thiomolybdate should be performed directly in the IR cell to exclude this possibility.

It is noteworthy that the bands of NO adsorbed on unsupported MoS_2 are also observed at lower wavenumbers, than for alumina-supported sample [37]. Higher metallic character of unsupported MoS_2 detected by the spectra of adsorbed CO and NO correlates with weaker acidity of its surface Mo sites, detected by pyridine, as compared with the supported catalyst. These results show that the modification of the acidic properties of MoS_2 is likely to be related to the interaction between the sulphide phase and the support, which modifies the electronic properties of the supported phase or results in different morphology of MoS_2 particles.

5. Conclusions

Unsupported MoS_2, despite strong absorption could be studied by means of IR spectroscopy. The surface of air-contacted MoS_2 is partially oxidised and contains adsorbed water, Mo=O groups, sulphate and thiosulphate-like anions. Most of these contaminations could be removed by evacuation while to eliminate the Mo=O groups, treating in H_2S–H_2 mixture is needed. Oxygen adsorption on the MoS_2 sample does not lead to noticeable changes in the spectrum, however ozone partially oxidises the surface already at 77 K with the formation of SO_2 molecules and Mo=O groups.

Pyridine, 2,6-dimethylpyridine, ethylene, CO_2, COS, SO_2 and CH_3SH exhibit only weak molecular adsorption on MoS_2. Basicity of surface sulphur atoms and the strength of acid–base pair sites is too low to form complex anions with the acidic molecules or to lead to dissociative adsorption of CH_3SH. No bands of protonated form or more or less strong coordination were detected by pyridine and 2,6-dimethylpyridine adsorptions. However, the surface was found to chemisorb ammonia with the formation, in particular, of NH_4^+ ions. Ammonium formation could be connected either with NH_3 ability to dissociate liberating protons, or with its higher basicity that favours its interaction with SH groups, which were not, however, detected directly in the IR spectrum of MoS_2 even after adsorption of H_2, H_2S or after heating in these gases or their mixture.

CO and NO chemisorption occurs on the coordinately unsaturated cation sites of MoS_2. The extent of back donation of molybdenum d-electrons is greater for unsupported sulphide, than for supported sulphide phase. These results demonstrate weaker acidic properties as well as higher metallic character of Mo sites of the unsupported MoS_2, as compared with those of MoS_2 supported on alumina. We can, thus, point to the important role of the support in modification of acid properties of the sulphide phase.

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