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Mechanism of the Adsorption of Organic Sulphur Compounds by Oxides and Zeolites

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Recent views on the mechanism of the separation of organic sulphur compounds by adsorption on oxides and on zeolites are discussed. 137 references

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I. INTRODUCTION

Interest in organic sulphur compounds has increased in recent years, mainly because of the increased importance of the extraction and treatment of sulphur- and high-sulphur-bearing petroleum and natural gas, of the extensive use of hydro- and thermocatalytic processes, and of the more stringent requirements for high-purity petroleum products produced by our increasing awareness of the need to combat atmospheric pollution.

At present the chemistry of natural organo-sulphur compounds (and in particular those associated with petroleum deposits) is being developed in two main directions: 1) improvements and developments in the methods of decomposing organo-sulphur compounds in order to produce high-quality fuels and oils[1,2], and 2) developments in the separation[3,4] and in the practical exploitation[5-7] of organic sulphur compounds. The latter activities offer the greatest interest in the chemistry of organic sulphur compounds, because they relate directly to the most basic problems of petroleum refining: to obtain high-quality products, to protect the environment from contamination, and to optimise our usage of natural resources. In recent years this work has become even more important because of the wide use of organic sulphur compounds isolated from petroleum products as special solvents, as very efficient media for the extraction of precious metals, as flotation reagents, as physiologically active materials, etc.[5,6]. In some cases[7] the prospect of replacing currently used, expensive synthetic products by naturally occurring organic sulphur compounds has been convincingly demonstrated.

Organic sulphur compounds found in petroleum include sulphides, disulphides, mercaptans, and thiophens[3]. The separation of these compounds, dissolved in multi-component mixtures of petroleum hydrocarbons, is laborious and difficult. Therefore much of the current research is aimed at effective methods of concentrating and separating organic sulphur compounds. Adsorption chromatography is one of the most promising methods of separating complex mixtures, and is widely used in this work[8,9].

Methods of controlling the surface properties of adsorbents by chemical modification have attracted a great deal of attention[8,9], and the theory of intermolecular interactions has been further developed[10]. However still further developments are needed in the chemistry of organic sulphur compounds. The main achievements in the past few years have been the development of new methods of separating complex mixtures on pure and on mixed oxides with variously modified surfaces. This review aims to discuss recent publications on the separation of natural and model systems on oxide adsorbents and on zeolites (including organic sulphur compounds). Studies of the mechanism of adsorption of sulphur-containing organic molecules by thermodynamic, spectral, and quantum-chemical methods will be specially considered.

II. ADSORPTION METHODS OF SEPARATION AND PURIFICATION

Both synthetic (zeolites, silica gels) and naturally occurring sorbents (fuller's earths, bauxites, other ores) are used in adsorption methods for the industrial production of oils, purification of gases from sulphur compounds, and separation of aromatic hydrocarbons from the products of the dehydrogenation of light petroleum fractions[11-13]. However these adsorbents have insufficient selectivity. Aromatic hydrocarbons, which are valuable constituents of fuels, are removed from the distillates together with the organic sulphur compounds. Hence one of the most important current problems is to develop adsorbents able to separate aromatic hydrocarbons selectively from organic sulphur compounds.

In the purification of fuels it is important not only to remove the sulphur compounds but also to desorb them without decomposition, in order to exploit any possible practical application. Recently discovered possibilities in the application of sulphur compounds from petroleum have shifted the problem into the area of very fine differentiations. It is essential to be able to identify the organic sulphur compounds, and to establish their structure, both by classifying them into groups (sulphides, disulphides, thiophens, mercaptans) and by identifying the individual members of a homologous series. The ideal solution is to use adsorbents with an activity related to the functional properties of the sulphur atom in different compounds. On the whole, oxide adsorbents offer most of the features needed for the separation of organic sulphur compounds, while zeolites have a number of advantages for more complete separation and purification[14-17].

The selectivity of adsorbents has been studied on synthetic mixtures of hydrocarbons and organic sulphur compounds, and also on various petroleum fractions. It has been shown that organic sulphur compounds are adsorbed on silica gel less strongly than nitrogen and oxygen compounds of analogous structure[18,19], but more strongly than paraffin–naphthene hydrocarbons or aromatic hydrocarbons[20]. The adsorbability of compounds in these classes decreases in the sequence:

nitrogen-containing, oxygen-containing, sulphur-containing compounds, aromatic hydrocarbons, paraffin–naphthene hydrocarbons. Within the organic sulphur compounds class the adsorption affinity increases in the sequence thiophens, aliphatic thiols, aliphatic disulphides, aromatic and cyclic thiols, aliphatic and cyclic sulphides[20,21]. Within each homologous series the adsorption affinity of the organic sulphur compounds decreases as the molecular weight increases.

Synthetic sorbents (silica gels, alumina gels, alumina-silicas, Mg, Fe, Cr, Al, Mo silicates) have been used successfully in the separation of the paraffin–naphthene part of petroleum fractions[22]. However the aromatic hydrocarbons are eluted together with the organic sulphur compounds. Extensive work[22-24] on the choice of adsorbents, eluents, and conditions for the separation of aromatic hydrocarbons from organic sulphur compounds has resulted in a modest enrichment of the chromatographic fractions in organic sulphur compounds, though the proportion of aromatic hydrocarbons in these fractions remains as high as 40–70%.[25] The difficulty of separating organic sulphur compounds from aromatic hydrocarbons is due partly to the similarity in the adsorption affinities of the two classes[21,24] and partly to the possibility of interactions between molecules in these classes[26,27]. Furthermore it has been shown that the conjugation of π-electrons with the unshared electron pairs of the hetero-atom can assist the separation (by adsorption) of a mixture of organic sulphides and sulphur-containing compounds of the aromatic type with a sulphur atom in the ring (thiophens). It is reported[21,28] that these mixtures can be separated fairly cleanly into sulphides and thiophens by repeated chromatography on silica gel.

Some success has been reported also in the separation of sulphides with normal and iso structures[29].

The influence of the surface chemistry of silica gel on the adsorption of organic sulphur compounds has been studied by several workers[30-38]. It has been shown that an increase in the concentration of water from 6 to 10 wt.% produces an almost total loss of the adsorption capacity of silica gel for organic sulphur compounds. Finely porous silica gels are more selective towards organic sulphur compounds than silica gels with larger pores[30]. Because of their greater selectivity, and of their greater surface area, finely porous silica gels offer a greater concentration and a higher yield of sulphur in the chromatographic fractions.

In spite of their greater surface area, silica gels and alumina gels have been found[33-38] to be inferior to alumina-silicas and to natural sorbents in their specific desulphurisation value. The adsorption capacity of silica gel towards organic sulphur compounds is markedly increased by deposition on the silica gel surface of iron[39] or nickel[33] oxides, nickel sulphide and phenyltrichlorosilane[32], or mercury acetate[40].

A comparative study of the adsorption capacity of metal silicates (Mg, Fe, Hg, Cr, Al, Mo) with different metal oxide to silica ratios towards organic sulphur compounds has shown that the most effective adsorbent is chromium silicate[32]. Up to 99.6% of the organic sulphur compounds from an oil fraction can be adsorbed on chromium silicate. Unfortunately the surface compounds undergo catalytic changes on the chromium silicate surface. Catalytic changes in the organic sulphur compounds have been observed also in the desulphurisation of fuels on alumina–silica catalysts[35,36,41-47]. Furthermore hydrogen bond formation between the SH group of mercaptans and the surface hydroxyl groups has been suggested[34].

On changing from adsorption on silica gel to adsorption on alumina an inversion of the relative adsorption affinities of organic sulphur compounds and aromatic hydrocarbons has been observed[48]. Unlike the selectivity of silica gel[49-52] towards organic sulphur compounds, that of alumina increases steeply with the temperature of the preliminary heat treatment[53]. With alumina baked at 700 °C up to 93% of the organic sulphur compounds could be removed from an oil fraction. Sulphides[54] and thiophens[55] can be separated more fully from petroleum fractions by successive chromatographic treatments on silica gel and on alumina.

Naturally occurring sorbents and alumina–silicas are used mainly for desulphurising petroleum products and natural gases[13,32-35]. The desulphurising power of bauxite can be increased by working at a higher adsorption temperature, which assists the chemisorption and the catalytic changes of the organic sulphur compounds. It has been shown[34] that sulphides and disulphides are fully desorbed from the bauxite surface, whereas mercaptans are oxidised to disulphides. The latter reaction is observed also on zeolites[13].

The use of manganese and iron ores[56] and of tripoli earth[18] for desulphurising petroleum products in the liquid and the vapour phase has shown that the adsorption capacity of these materials towards organic sulphur compounds is relatively low. In some cases the effectiveness of the natural sorbent tripoli earth has been improved by acid–alkali activation.

Zeolites can be used to purify petroleum products from sulphur-containing constituents and to separate these impurities[57,58]. However this method of sulphur removal is most widely used for gaseous media[13,59,60]. Natural gas can be purified from hydrogen sulphide and other sulphur gases on zeolites.

Several variants of analytical and preparative gas–liquid chromatography[3,23,24,61] are used for identifying and classifying into groups the organic sulphur compounds obtained from petroleum products. The method offers effective separation into groups in the case of the low-molecular-weight organic sulphur compounds obtained from benzine and kerosine distillates[62-64]. However the results are directly applicable to the analysis of heavier fractions, because of the volatility of the liquid phase at the relatively high temperatures used in the chromatographic analysis. In this context the correct choice of adsorbent for analysis and preparative separation by liquid–adsorption chromatography is most important[65,66].

The method of chromatography in a thin layer of adsorbent has been widely used to monitor rate and extent of reaction in the synthesis of sulphides[67] and in studies of the reactions and transformations of sulphides[67,68].

III. ISOTHERMS AND HEATS OF ADSORPTION

The isotherms and the heats of adsorption provide important information on the mechanism of the interaction of organic sulphur compounds with the adsorbent surface. Adsorption isotherms have been measured mainly for low-molecular aliphatic sulphides[35,50-52,69], some aromatic (diphenyl and dibenzyl) sulphides[36], and thiophen[70-72] on silica gels, on mixed oxides, and on zeolites and naturally occurring sorbents.

A detailed study has been made[70-72] of the isotherm for the adsorption of thiophen from solutions in heptane and in benzene. As shown in Fig.1, in the low-coverage region the adsorption of thiophen by 13X zeolite is an order of magnitude greater than adsorption by silica gel or alumina. The difference on the adsorption of thiophen on silica gel and on alumina is relatively small.

A study of the adsorption isotherms of thiophen and of benzene on silica gel, alumina gel, and alumina[70] showed that the adsorption of thiophen (for the same relative pressure) is greater (by ~10%). The difference in adsorption is ascribed to the smaller size of the thiophen molecule (38 Å^2, as compared with 41 Å^2 for the benzene molecule). However the difference between the specific interaction energies of thiophen

(2.3 kcal mole^{-1}) and benzene (1.7 kcal mole^{-1}) with the silica surface suggests that the adsorption may be affected also by the interaction of the hydroxyl groups with the sulphur atom.

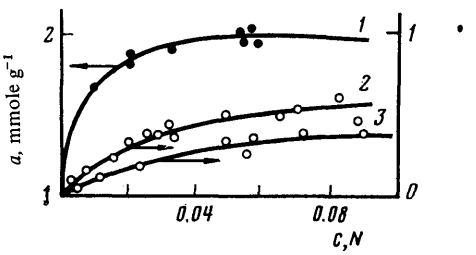


Figure 1. Isotherms for the adsorption of thiophen from hepaten on: *1*) 13X zeolite, *2*) silica gel, and *3*) aluminium oxide (*c* is the equilibrium concentration, *a* is the adsorption).

The influence of the chemistry of the adsorbent surface on the type of interaction can be studied by comparing the heats of adsorption of thiophen on mixed oxides, on silica gel, and on naturally occurring sorbents[49,74,75]. The cobalt–molybdenum oxide catalyst gives the highest interaction energy for thiophen molecules (15.5 kcal mole^{-1}, as compared with 8.4 kcal mole^{-1} on silica gel). Changes in the chemistry of the catalyst surface (by sulphidation) and of the silica gel (by dehydroxylation) are always accompanied by changes in heat of adsorption. However the largest effect is observed after sulphidation of the cobalt–molybdenum oxide catalyst: the heat of adsorption of thiophen on a sulphidised sample (6.6 kcal mole^{-1}) is close to the value obtained for a dehydroxylated sample of silica (6.1 kcal mole^{-1}).[49]

The effect of dehydroxylation of Aerosil[49] and silica gel surfaces[50–52] on the interaction energy of adsorbed molecules has been observed also for other classes of sulphur compounds. Progressive dehydroxylation of an Aerosil surface (by heating the sample at 300, 500, and 900 °C) lowers the heats of adsorption of sulphides, disulphides, and thiophens. By increasing the level of dehydroxylation of the surface we can decrease the sensitivity of the heat of adsorption to the chemical properties of the adsorbed molecules, confirming the important contribution of the sulphur atom to the specific interaction energy with the hydroxyl groups.

The nature of the interaction of organic sulphur compounds with the OH groups of the silica surface is reflected by the specific component of the heat of adsorption ΔQ.[49] Relatively low values of ΔQ (2.3–4.8 kcal mole^{-1}) suggest interaction through a hydrogen bond. Saturated aliphatic hydrocarbons have almost identical specific interaction energies (3.9–4.4 kcal mole^{-1}), somewhat lower than the specific interaction energy of cyclic sulphides (4.8 kcal mole^{-1}). It is interesting to note that disulphides have a specific interaction energy (3.0–3.2 kcal mole^{-1}) 1.5 times lower than that of sulphides. Even lower ΔQ values (2.6–2.2 kcal mole^{-1}) are reported[76] for compounds of the thiophen series, suggesting that the contribution of the sulphur atom to the interaction is weakened by the conjugation of its unshared electron pairs with the π-electrons of the thiophen ring.

The effect of dehydroxylation of the silica gel surface (by baking the sample at 200 and 500 °C) on the adsorption of low-molecular sulphur compounds has been studied by Ross and coworkers[50–52]. The fast desorption of hydrogen sulphide from the surface confirms that adsorption is physical, as reported also in Refs.69 and 77. The adsorption of methyl and ethyl mercaptan, and of dimethyl sulphide, is also reversible[50]. The energy of the specific interaction of methyl mercaptan with the hydroxyl groups of silica gel is ~2.2 kcal mole^{-1}.[50]

It has been suggested that the difference in the nature of the interactions of SO_2,[50] H_2S, CH_3SH, C_2H_5SH, and $(CH_3)_2S$ [51,52] with the silica gel surface is determined by the symmetry and the character of the spatial localisation of the orbits occupied by the unshared electron pairs. This explanation is consistent with the formation of complexes of methyl mercaptan and dimethyl sulphide with diborane [$CH_3SH.BH_3$; $(CH_3)_2S.BH_3$]. This type of complex is not formed by hydrogen sulphide[78].

When organic sulphur compounds are adsorbed on silica gel at 150 °C the initial heat of adsorption is fairly high[51] (>30 kcal mole^{-1}): this is probably due to the presence of impurities, undergoing surface reactions.

The adsorption of methyl mercaptan, ethyl mercaptan, dimethyl sulphide, and hydrogen sulphide on γ-Al_2O_3 baked at 700 °C has been studied[79] at 150 °C. Hydrogen sulphide is adsorbed less readily than the other compounds. Unlike the adsorption of methyl and ethyl mercaptan and dimethyl sulphide, the adsorption of hydrogen sulphide leaves a residue of elemental sulphur on the γ-Al_2O_3 surface, which proves the reality of surface decomposition reactions.

The heat of adsorption of hydrogen sulphide falls from 31.5 to 16.3 kcal mole^{-1} as the surface coverage is increased from 0.05 to 0.34 mmole m^{-2}. Similar variations were observed for the adsorption of hydrogen sulphide on γ-Al_2O_3 at 300 and 464 °C, when the heat of adsorption was 25 and 38 kcal mole^{-1} for surface loadings of 0.17 and 0.114 mmole m^{-2} respectively[80]. The heats of adsorption (Q, kcal mole^{-1}) of organic sulphur compounds on silica gel[52] and alumina[79] surfaces dehydroxylated at different temperatures are listed below (for a surface coverage of 1.4 mmole m^{-2}):

t, °C	Silica gel			γ-Al_2O_3
	240	550	700	700
Hydrogen sulphide	9.8	7.3	5.8	16.8
Methyl mercaptan	11.5	10.5	6.5	16.5
Ethyl mercaptan	12.3	11.7	9.7	18.4
Dimethyl sulphide	17.5	14.7	12.3	20.7

The higher heats of adsorption on γ-Al_2O_3 than on silica gel (at the same coverage) are ascribed to the interaction of the organic sulphur compounds with both the surface hydroxyl groups and the Lewis-acid centres of γ-Al_2O_3.

Gal'pern and coworkers[32] describe a comparative study of the adsorption of dibenzyl sulphide, diisopentyl sulphide, and biphenyl from solutions in iso-octane on a magnesium silicate adsorbent and on coarsely porous silica gel modified by nickel sulphide and phenyltrichlorosilane. The largest difference in the adsorptions of the sulphides and of biphenyl was observed on silica gel coated with a layer of nickel sulphide[32]. The largest increase in the adsorption capacity of tripoli earth[18] for dibutyl sulphide was achieved by acid–base activation (with a mixture of 12% NaOH and 20% HCl) of the surface of the naturally occurring sorbent.

Studies of the adsorption isotherms of organic sulphur compounds on zeolites have shown that the nature of the interaction is determined by the geometric and by the chemical structure of both the adsorbed molecules and the zeolite surface. It is reported[13,81] that hydrogen sulphide and mercaptans can be removed by CaA zeolites, and cyclic organo-sulphur compounds by type X zeolites: the difference is due mainly to steric hindrance during adsorption. The largest effect on the amount of adsorption is produced by the

type and extent of cation exchange. Thus it is shown[17] that the adsorption of sulphur compounds is more extensive on zeolites containing alkaline-earth metal cations than on NaY zeolite. However the adsorption does not increase regularly as the Na^+ cations are replaced by univalent and bivalent metal cations[82-86]. The amount of exchange giving optimum adsorption depends on the type of molecule being adsorbed, and for organic sulphur compounds (ethyl propyl sulphide, di-n-butyl sulphide, thiophen, alkyl mercaptan, thiophenol) the optimum varies between 25 and 70%.

The increased adsorption capacity of zeolites as a result of ion exchange is due to the creation on the zeolite surface of a distribution of cations with different charges which is favourable to adsorption. The adsorption capacity of NaA and NaX zeolites and their magnesium-substituted samples can be increased also by pre-adsorption of a controlled amount (between 1 and 3.5 wt.%) of H_2O, NH_3, or CH_3NH_2.[15,87] The exchangeable cations are located in different sites of the zeolite network, and site exchange is possible during adsorption[88,89].

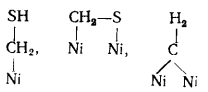
The activity of zeolites towards organic sulphur compounds is substantially increased by decationation of the zeolite[90]. In this case the activity increases monotonically with the extent of decationation. By using this type of sample thiophen can be extracted almost quantitatively from dilute solutions in benzene.

IV. SPECTROSCOPIC STUDY OF ADSORPTION

The optical method most widely used to study the hydroxyl covering of oxide surfaces and its role in adsorption interactions is infrared spectroscopy[91-93]. It was first applied to studies of the adsorption mechanism of organic sulphur compounds by Eyring and Wadsworth[94], who explained the spectra of n-hexyl mercaptan on zinc oxide, sulphide, and silicate, and also on willemite ($ZnSiO_4$), by postulating the surface reaction

$$-Zn-OH + HSR \rightarrow -Zn-SR + H_2O.$$

From the spectra of hydrogen sulphide, methyl mercaptan, ethyl mercaptan, and diethyl sulphide adsorbed on nickel (20%) supported on silica gel it was concluded[95] that surface compounds of the following types are formed:



Analogous structures were proposed for chemisorbed ethyl mercaptan and diethyl sulphide.

The interaction of sulphides, disulphides, mercaptans, and thiophens with the surface hydroxyl groups of silica samples baked at 200 and 500 °C has been investigated by infrared spectroscopy[96-99]. It was found that the organic sulphur compounds interact with the hydroxyl groups of the silica surface, as shown by the decreased intensity and the shift of the absorption band at 3750 cm^{-1} (which characterises the stretching vibrations of the free OH groups). For the sulphides the absorption band of the perturbed OH groups lies at 3320–3390 cm^{-1}, for the mercaptans at 3310–3475 cm^{-1}, for the disulphides at 3340–3530 cm^{-1}, and for the thiophens at 3600–3630 cm^{-1}.

The smallest shifts in the absorption band for the stretching vibrations of the surface hydroxyl groups are observed after adsorption of compounds of the thiophen series (thiophen, 3-propylthiophen, 2,5-diethylthiophen, which give shifts of 116, 140, and 150 cm^{-1} respectively). These small values suggest a weak participation in adsorption interaction by the sulphur atom, due to the conjugation of its unshared electron pairs with the π-electrons of the thiophen ring.

It has also been shown that organic sulphur compounds of the aromatic type can interact with hydroxyl groups both through the unshared electron pairs of the sulphur and through the π-electron system. The absorption band at 3640 cm^{-1} characterises the interaction of the OH groups with the benzene ring, and the absorption band at 3550 cm^{-1} their interaction with the sulphur atom of thiophenol (Fig. 2). The shift of the absorption band of the surface hydroxyl groups increases in the same sequence as the specific interaction energy[49]. In homologous series of organic sulphur compounds the quantity $\Delta\nu_{OH}$ varies in direct proportion to the ionisation potential. The observed spectral[97-99] and energy parameters[49] of the adsorption process lead to the conclusion that organic sulphur compounds can be arranged in the following series as regards their affinity towards hydrogen bond formation with surface hydroxyl groups: sulphides > mercaptans > disulphides > thiophens.

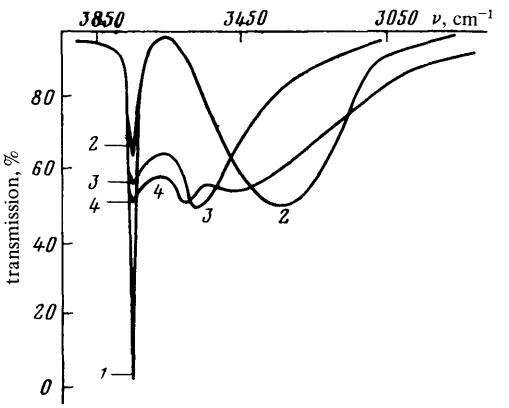


Figure 2. Changes in the spectrum of the surface hydroxyl groups of Aerosil (*1*) caused by the adsorption of organic sulphur compounds: *2*) dipropyl sulphide, *3*) thiophen, *4*) thiophenol (spectrum *1* was obtained after vacuum baking the sample for 5 h at 500 °C).

We should note that organic sulphur compounds behave as weaker donors than oxygen compounds of the same structure when forming hydrogen bonds with surface hydroxyl groups. This effect can be ascribed (as in the formation of hydrogen bonds with proton-donating solvents[100,101]) to the difference in electronic structure between the sulphur and the oxygen atom.

The i.r. spectra of sulphides, disulphides, mercaptans, and thiophens adsorbed on alumina[96,102-106] or on mixed oxides (Al_2O_3, NiO, MoO_3)[95,106-108] show that surface reactions can occur in parallel with the physisorption of organic sulphur compounds as a result of the formation of co-ordination bonds with the electronically unsaturated surface centres through the sulphur atom.

It has been shown also[97,105] that organic sulphur compounds adsorbed on alumina can interact with the hydroxyl groups of the surface through the formation of a hydrogen bond. The changes in frequency of the OH absorption bands ($\Delta\nu_{OH}$,

cm^{-1}) caused by adsorption on silica and on alumina are listed below:

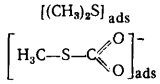
Compound	Thiophan	Dimethyl sulphide	Dimethyl disulphide	Thiophenol	Thiophen
SiO_2[49]	415	369	215	200	116
γ-Al_2O_3[86]	180	130	120	130	100

The shifts in the absorption bands of the structural hydroxyl groups produced by the adsorption of aliphatic and cyclic sulphides and disulphides and of aliphatic mercaptans on alumina are less substantial than the shifts produced in silica. We note that the shift $\Delta\nu_{Al-OH}$ is less sensitive to the state of the sulphur atom in the molecule. Thus on changing from thiophan to thiophen the shift changes by ~3.6 for adsorption on silica and only by 1.8 for adsorption on alumina, which may be explained, as in the case of the adsorption of ethers[91], by the amphoteric nature of the groups in aluminium oxide. However, in contrast to adsorption on pure silica, we observe the formation of surface compounds containing CH_2 and CH_3 groups (with absorption bands at 2890, 2950, and 2988 cm^{-1}).

Analogous spectral changes in the region 2700–3200 cm^{-1} are observed during the interaction of thiophen with the surface of nickel[95], montmorillonite[76], cobalt molybdate, and molybdenum or germanium sulphide[107,108], and also zeolites of type HY,[109] NaX, CaX,[110] NaY, CaY, and CuNaY.[111,112]

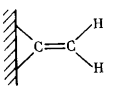
The spectra of sulphides, mercaptans, disulphides, and thiophens adsorbed on alumina[102-106,112,113] and on the oxides of molybdenum, manganese, vanadium, and chromium[114,115] show absorption bands in the region of 1290–1600 cm^{-1} (with maxima at 1290, 1470, 1495, and 1600 cm^{-1}) even at 20 °C. The appearance of these bands is believed to result from the formation of thiocarbonate and thiocarboxylic acid groups on the surface[93,116,117], and of groups with an oxidised sulphur atom (see Table). The absorption bands at 1290, 1495, and 1600 cm^{-1} persist in the spectrum at high desorption temperatures (400–500 °C), demonstrating the high thermal stability of these surface compounds.

Structures formed by the adsorption of dimethyl sulphide on metal oxides (Si, Al, Mo, Cr, Mn, V).[114]

Structure No.	Structure	Formation temp., °C	Decomposition temp., °C
(I)	$[(CH_3)_2S]_{ads}$	20	100–150
(II)		20	450
(III)	$[(CH_3)_2SO]_{ads}$	20	150–200
(IV)	$[(CH_3)_2SO_2]_{ads}$	20	150–200
(V)	$[CH_3SO_3]^-_{ads}$	20–150	450
(VI)	$[HCOO]^-_{ads}$	20–250	450
(VII)	$(SO_4)^{2-}$	150	400–500

The breakdown of the surface structures produced by chemisorbed organic sulphur compounds yields hydrogen sulphide and unsaturated hydrocarbons. Thus on raising the desorption temperature of thiophen adsorbed on ultramarine[119] we observe the appearance of a new spectral band at 2630 cm^{-1} (for desorption at 100 °C), which splits into two bands (2500 and 2650 cm^{-1}) for desorption at 200 °C, accompanied by a new absorption band at 2690 cm^{-1}, characteristic of adsorbed hydrogen sulphide (2679 cm^{-1}). All three absorption bands disappear at 300 °C. Similar adsorption bands were observed[108] during the desorption of thiophen, water, and hydrogen adsorbed on MoS_2 and GeS. It is suggested[108,119] that the absorption bands at 2500–2700 cm^{-1} correspond to the vibrations of the S–H bonds of surface compounds. The appearance of absorption bands at 2850, 2960, and 3045 cm^{-1} is ascribed to the formation of but-1-ene or but-2-ene.

The absorption bands at 3050, 3140, and 3150 in the spectrum are assigned to HC ≡ CH surface groups, or to the structure



Davydova and coworkers[114,115] observed the oxidation of dimethyl sulphide on molybdenum, manganese, vanadium and chromium oxides in the presence of surface oxygen. The evidence was the appearance in the spectrum (Fig. 3) of absorption bands at 1045, 1145, and 1320 cm^{-1}, typical of the stretching vibrations of the SO group in adsorbed dimethyl sulphoxide[120] and dimethyl sulphone[121] [structures (III) and (IV)]. Raising the adsorption temperature (to 150 °C) caused the formation of surface structures [(V) and (VII)] with a sulphur atom in a higher state of oxidation, as shown by the appearance of absorption bands at 1045, 1145, and 1275 cm^{-1}, characteristic of the vibrations of the S–O bond in sulphites, sulphates, and sulphonates[122] [structure (VII)]. The formation of absorption bands at 1360 and 1380 cm^{-1} (stable up to 450–500 °C) in the spectrum of dimethyl sulphide adsorbed on chromium oxide at 250 °C is ascribed to formate ions on the surface [structure (VI)].

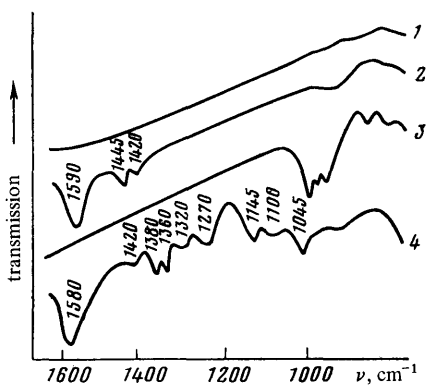


Figure 3. I.r. absorption spectra of chromium oxide: *1*) activated in vacuum at 250 °C, *2*) after adsorption of dimethyl sulphide at 250 °C, *3*) activated in oxygen at 250 °C, *4*) adsorption of dimethyl sulphide at 250 °C on a sample activated in oxygen.

Thiocarboxylate and thiocarbonate groups, and groups with an oxidised sulphur atom, are formed also during the adsorption of sulphur compounds on alumina, and on NaY, CaY, NaCay, and CuNaY zeolites[110-112,123,124]. The adsorption of thiophen on zeolites with exchanged cations of the transition metals produces complex compounds[110]. More

extensive decomposition of the sulphur-containing molecules occurs when the univalent cation is replaced by a bivalent cation. It is found[109,123] that the adsorption mechanism is strongly influenced by the protonic acidity of the zeolite. Thus on HY zeolite[109,123] (but not on NaY zeolite) thiophen undergoes chemical reactions involving the breaking of C–S bonds and the formation of surface compounds containing S–H bonds (2380 cm^{-1}) and unsaturated (3100 cm^{-1}) or saturated (2800–3000 cm^{-1}) C–H bonds. These results are relevant to our understanding of the mechanism of catalytic hydrodesulphurisation processes for organic sulphur compounds.

In recent years adsorption and spectra methods have been combined to demonstrate the important role of impurity centres during adsorption on silicas[91,125,126]. These results help us to understand the mechanism of adsorption, because technical grades of siliceous adsorbents always contain impurities of aluminium, iron, and other oxides. The effect of aluminium, boron, cadmium, titanium, and iron oxides on the interaction of organic sulphur compounds with silica has been studied in detail[96,127,128]: it was found that the sulphur compounds interact by the hydrogen bond mechanism with the silanol hydroxyl groups and with OH groups bound to impurity metal atoms. Furthermore the presence of impurity centres leads to chemisorption and to the formation of surface complexes, with partial decomposition of the sulphur compound.

U.v. spectroscopy has been used[129,130] for the analysis of charged forms of adsorbed molecules such as carbonium ions. We have studied[131] the u.v. spectra of thiopehn, thiophan, thiophenol, benzothiophen, 2- and 3-methylbenzothiophens, and 2-methyl-2,3-dihydrobenzothiophen adsorbed on alumina and on alumina-silica. Adsorption of these molecules on alumina does not produce any charged forms up to 300 °C, but charged forms are produced by adsorption on alumina–silica at temperatures above 100 °C.

V. QUANTUM-CHEMICAL CALCULATIONS OF ADSORPTION COMPLEXES

The methods of quantum chemistry are being used increasingly in the study of adsorption mechanisms[132–134]. In this approach the conventional semi-empirical procedures of quantum chemistry are applied to calculations on models which include an adsorbed molecule and an atom from the adsorbent surface (cluster).

Relying on the simple Hückel method, Stodoiski and coworkers[135] used the interaction between organic sulphur compounds and a transition metal surface to calculate adsorption models, allowing for the possible formation of surface structures without dissociation of the adsorbed molecules and also for the formation of sulphide layers by the reactions

$$R{-}S + M \rightarrow M \ldots S{-}R, \quad (1)$$

$$R{-}S + M \rightarrow R + MS, \quad (2)$$

where R is a hydrocarbon radical and M is a metal atom.

It was found that the stability of the S–M bond decreases as the electronegativity of the metal increases. The reaction between the organic sulphur compound and metals was shown to weaken the C–S bond and to strengthen the adjacent C–C bond. A significantly large decrease in the population of the C–S bond indicates the possibility of dissociation of the adsorbed molecules. By calculating the energy of reaction (2) it was shown that dissociation is most likely with thiophenol, hexamethylene sulphide, and vinyl mercaptan.

We have also used[136] the extended Hückel method in calculations on adsorption complexes containing hydroxyl groups, modelling the interaction of thiophen and dimethyl sulphide with oxide surfaces. The change in the properties of the hydroxyl group on different oxide surfaces was modelled by assigning a predetermined charge to the hydroxyl group. The CNDO/2 method was used[137] to show that the charge on the proton can be correlated with the acidic properties of the hydroxyl groups. Recent calculations[136] have shown that better agreement with experimental data[49,96,97] can be expected for models including uncharged hydroxyl groups.

The substantial stabilisation and strong change in the charge on the sulphur atom in the complexes produced by thiophen and dimethyl sulphide with a positively charged hydroxyl group are ascribed to the formation of bonds with charge transfer from the sulphur atom towards the hydroxyl group. In the model complexes between dimethyl sulphide and the hydroxyl group the weakening of the O–H bond is more marked than in the corresponding thiophen complexes. These results are consistent with the more substantial shift of the surface hydroxyl absorption band at 3750 cm^{-1} [96,97] and with the greater specific interaction energy for the adsorption of dimethyl sulphide on silica (360 cm^{-1} and 3.2 kcal $mole^{-1}$ respectively) as compared with the adsorption of thiophen (120 cm^{-1} and 2.3 kcal $mole^{-1}$ respectively). The calculations suggest that interaction of the organic sulphur compounds with two surface hydroxyl groups may be preferred on energy grounds. Hence a planar orientation of the molecules on the silica surface is probably the most favourable.

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Thus adsorption-chromatographic methods will be used increasingly for the separation of naturally occurring organic sulphur compounds without changing their structure, and also for developing new methods of classifying these compounds by group (sulphides, disulphides, mercaptans, thiophens) and according to structural features within a homologous series.

The solution of important problems in the chemistry of the sulphur compounds occurring in petroleum depends on a correct understanding of the mechanism by which organic sulphur compounds interact with adsorbents of different types: this understanding is needed in the search for new modifying additives for inorganic sorbents, aimed at increasing their efficiency and at extending the practical utilisation of sulphur compounds from petroleum in the national economy.

This review has shown that the application of thermodynamic and spectral methods (together with quantum-chemical calculations) to adsorption studies can assist our understanding of the interactions taking place on the surface.

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