Russian Chemical Reviews **62** (2) 105–120 (1993)
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UDC 541.183

Use of IR spectroscopy in studies of catalysts based on molybdenum heteropoly compounds supported on oxides

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Contents

I. Introduction	105
II. Molybdenum heteropoly compounds	105
III. Supported molybdenum oxide catalysts. Formation, identification, and acidic properties of surface compounds	110
IV. Thermal stability of molybdenum compounds, decomposition mechanism, role of modifiers	116
V. Conclusions	118

Abstract. Experimental data on the use of IR spectra to identify compounds formed on the surface of various supports during the deposition of heteropoly compounds are reviewed. The spectral properties of the heteropoly compounds are analysed according to their type, to the character of the central ion, and to the form of the support. The first attempts to study the acidic properties of systems of this type are reported. The prospects of identifying the compounds formed on the surface of the carriers during the preparation of supported catalysts containing molybdenum or tungsten are examined. The bibliography includes 124 references.

I. Introduction

Heteropoly compounds (HPC) [heteropoly acids (HPA) and their salts] are now widely used in heterogeneous catalysis. They are effective catalysts of important chemical processes,[1–4] and they are also convenient as model catalytic systems, offering a useful combination of acid and oxidation–reduction properties which allows the composition and structure of the catalytically active centre to be strictly determined. Furthermore the HPC allow controlled variations of both the acidic and the oxidation–reduction function of the catalytic system, and in this sense they are superior to the zeolites.

The heteropoly compounds of molybdenum are good starting compounds for the preparation of multicomponent catalysts containing molybdenum, which includes most of the heterogeneous catalysts used in a variety of chemical processes such as partial oxidation.[4,5] Indeed, these compounds make possible the preparation of previously stipulated and exactly defined catalyst compositions with good mixing and complete interaction of the components, which allow the function of each of the components to be clearly displayed.

The role of HPC as precursors of active and selective catalysts has been pointed out more than once[5,6] in published work. the composition of many well known (including industrial) catalysts containing molybdenum probably included compounds of the HPC type. These can be formed in the course of the catalytic reaction (at least, on the surface of the heterogeneous system, where they cannot be observed by traditional methods such as X-ray diffraction analysis).

Supported catalysts offer several advantages,[7] of which the most important for HPC are probably a high mechanical strength and a developed specific surface. Furthermore a great saving in the expensive molybdenum compounds can be achieved by using supported catalysts. It has been shown[8] that in oxide catalysts the carrier can experience strong chemical interactions with the supported compound.

Published data on the character of the interaction of supported heteropoly compounds with the surface of the carrier are few.[8] It has been shown that when ammonium paramolybdate (APM) $(NH_4)_6Mo_7O_{24}$ is supported on carriers such as SiO_2, TiO_2, and Al_2O_3 the Si–Mo,[9] Ti–Mo,[10] and Al–Mo heteropoly compounds[11,12] can be synthesised on the surface of the catalysts under the influence of the cations of the support. These compounds are stable up to high temperatures. We may therefore assume that compounds of this type containing molybdenum as the active component will find extensive application as catalysts for the partial oxidation of hydrocarbons.[7] Therefore a more general formulation of the published information, a critical assessment of the reliability with which these compounds have been identified, and a determination of their properties are currently important problems.

II. Molybdenum heteropoly compounds

Traditional phase analysis methods, including X-ray phase analysis (XPA), have not been applied to HPC because of the dehydration of these materials and of the small content of the active component in supported catalysts. Vibrational spectroscopy offers some important advantages in these systems.[8–11,13] However, one of the difficulties in the study of supported systems is that the spectrum of the support usually overlaps the spectral region of the active component, making the latter difficult to resolve. Therefore the spectrum of the active component is often revealed by a procedure based on compensation for the spectrum of the support.[8–11,14]

1. IR spectra of massive heteropoly compounds

The IR spectra of HPC have been studied in detail. They adequately characterise HPC belonging to different structure types. In Fig. 1 we show the IR spectra of massive HPC containing 6 and 12 Mo atoms (Mo_6-HPC and Mo_{12}-HPC). In the spectra of Mo_6-HPC (spectra *4–6*) at 400–700 cm^{-1} we find strong absorption bands near 650 (ν_{as}) and 450 cm^{-1} (ν_s), assigned to the vibrations of the Mo–O–Mo bridging bonds.[15–17]

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Received 14th May 1992
Uspekhi Khimii **62** (2) 118–134 (1993); translated by J I Carasso

Furthermore the vibrations of the Mo=O multiple bonds[15-17] can be seen at 880–950 cm^{-1}. We should stress the difference between the spectra of the Mo_6-HPC in which the central atoms are triply charged (Fe^{3+} or Al^{3+}) ions (spectra *5* and *6*) or doubly charged ions (Cu^{2+}, Co^{2+}, spectrum *4*).† In the latter case the absorption bands assigned to $\nu_{Mo=O}$ and $\nu_{Mo-O-Mo}$ are shifted towards lower frequencies (925 and 635 cm^{-1} respectively) in comparison to the Al–Mo–HPC (945 and 665 cm^{-1}) and Fe–Mo–HPC spectra (945 and 645 cm^{-1}).

In the IR spectra of Mo_{12}- and $Mo_{11}Co$-HPC (Fig. 1, spectra *1–3*)‡ strong absorption bands are not found at 400–700 cm^{-1}, in contrast to the spectra of Mo_6-HPC. According to generally accepted suggestions[15-17] the IR absorption spectra of Mo_{12}-HPC in the 900–1000 cm^{-1} region correspond to the vibrations of the Mo=O end bonds (for example, the 965 cm^{-1} band in the spectra of P–Mo-HPC, spectrum *2*), whereas at 700–900 cm^{-1} we observe the stretching vibrations of the Mo–O–Mo bonds (absorption band at 780 cm^{-1} in the spectrum of Si–Mo-HPC, spectrum *1*). We note that the replacement of one molybdenum cation in the $SiMo_{12}O_{40}$ heteropoly anion by a different transition metal ion (mixed HPC, spectrum *3*) shifts the absorption band at 900–1000 cm^{-1} towards lower frequencies by 20–30 cm^{-1}. We also observe the appearance of an absorption at 720–730 cm^{-1}, which is not seen in the spectra of the Si–Mo-HPC.[18-20]

Thus the IR spectra of Mo_6-HPC in the region of 400–700 cm^{-1} differ markedly from those of Mo_{12}-HPC, whereas the IR spectra of mixed HPC at 700–1000 cm^{-1} differ from those of Si–Mo_{12}-HPC. These differences in the IR spectra of HPC belonging to different structure types allow the behaviour of the HPC supported on oxide carriers to be studied by IR spectroscopy.

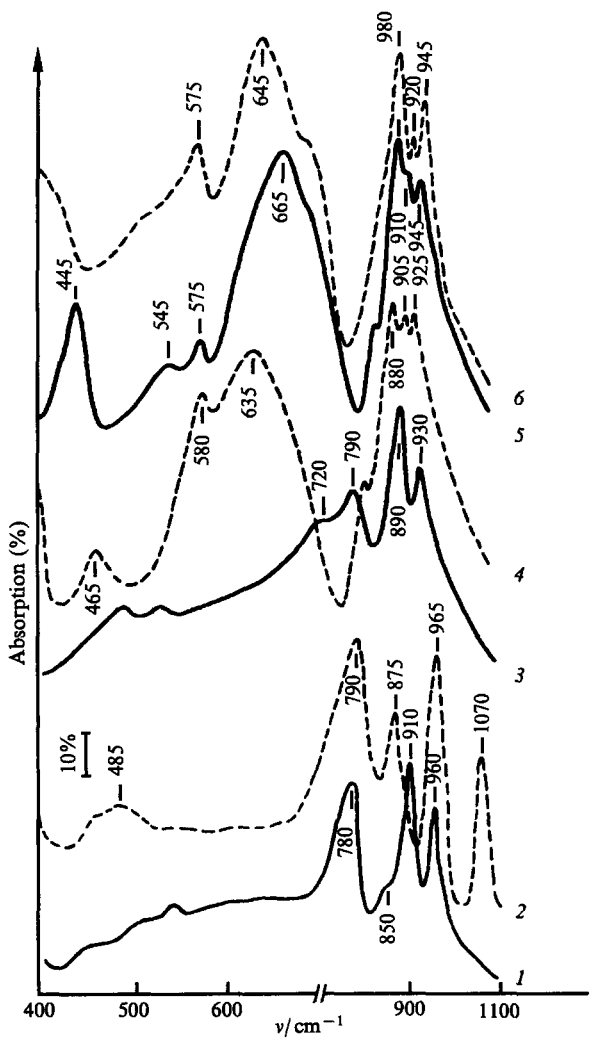


Figure 1. IR spectra of massive HPC dried at 373 K:
1) Cu_2SiMo_{12}, *2*) $Cu_{2/3}PMo_{12}$, *3*) $(NH_4)_6SiMo_{11}Co$, *4*) $(NH_4)_4CoMo_6$, *5*) $(NH_4)_3AlMo_6$, *6*) $(NH_4)_3FeMo_6$.

2. IR spectra of supported heteropoly compounds and effect of the support on their structure

The IR spectra of catalysts prepared by depositing the HPC $(NH_4)_{6-n}M^{n+}Mo_6$ (M = Cu^{2+}, Co^{2+}, Fe^{3+}) on SiO_2 are almost identical (spectra *3–5* of Fig. 2), but they differ markedly from the spectra of the unsupported (bulk) Mo_6-HPC of the transition metals (spectra *4–6* of Fig. 1): the strong absorption bands at 400–700 cm^{-1} are replaced by strong bands at 730–970 cm^{-1}, which are not found in the spectra of bulk Mo_6-HPC. As was stated above, these spectral features are also found in Mo_{12}-HPC and in mixed HPC. Comparing the spectra of Mo_6-HPC supported on SiO_2 (spectra *3–5* of Fig. 2) with the spectra of Mo_{12}- and $Mo_{11}Co$-HPC shows an analogy with the IR spectrum of the mixed $Mo_{11}Co$-HPC (spectrum *3* of Fig. 1). This suggests that when the Mo_6-HPC of copper, cobalt, and iron are supported on SiO_2 they become rearranged into mixed Si–Mo–M-HPC, i.e. molybdenum ions are replaced by transition metal cations.

The IR spectra of samples prepared by supporting $(NH_4)_4CuMo_6$ (spectrum *7* of Fig. 2) and $(NH_4)_4CoMo_6$ (spectrum *8* of Fig. 2) on Al_2O_3 are almost identical, and differ significantly from the spectrum of unsupported $(NH_4)_4CoMo_6$ (spectrum *4* of Fig. 1): for example, their $\nu_{Mo=O}$ and $\nu_{Mo-O-Mo}$ frequencies are shifted (by 20 and 30 cm^{-1} respectively) towards longer wavelengths as compared with the absorption bands at 925 and 635 cm^{-1} observed for the bulk compounds. These shifts in the position of the IR absorption bands can be used to distinguish the Mo_6-HPC of doubly charged cations from the HPC of triply charged cations. Comparing the spectra of these catalysts (Fig. 2, spectra *7* and *8*) with the spectrum of the NH_4 salt of the Al–Mo-HPA (where HPA is a heteropoly acid) supported on Al_2O_3 (Fig. 2, spectrum *6*) shows marked similarities, with coinciding maxima of the most characteristic absorption bands. This suggests that the deposition of the molybdenum heteropoly compounds of Cu and Co on Al_2O_3 causes the formation of Al compounds, involving the Al surface atoms of the support. Under these conditions the copper and cobalt cations usually continue to be the salt formers. The change in colour of the samples (from blue to green for the copper HPC and from light brown to lilac for the cobalt HPC) confirms the change in state of the Mo_6-HPC of copper and cobalt when supported on Al_2O_3.

An analysis of the IR results for samples prepared by supporting $(NH_4)_3FeMo_6$ on Al_2O_3 shows that in this case $FeMo_6O_{24}H_6^{3-}$ is converted into $AlMo_6O_{24}H_6^{3-}$. In the IR spectra of these catalysts in the $\nu_{Mo-O-Mo}$ region (spectrum *9* of Fig. 2) the characteristic absorption of the Fe–Mo-HPC at 645 cm^{-1} (spectrum *6* of Fig. 1) is replaced by an absorption band at 665 cm^{-1}, proper to the spectrum of the Al–Mo-HPC (spectrum *5* of Fig. 1), and furthermore an absorption at 445 cm^{-1} (belonging to the spectrum of Al–Mo-HPC, spectrum *5* of Fig. 1) is also seen. However, at 880–950 cm^{-1} these two compounds behave identically.

Thus the MMo_6-HPC (where M = Cu, Co, Fe) are unstable. When supported they react with the oxide carrier, and they decompose even at the drying stage. On an SiO_2 surface the silicon ions of the carrier form mixed Si–Mo–M-HPC in which transition metal cations replace molybdenum ions:

$$(NH_4)_{6-n}M^{n+}Mo_6O_{24}H_6 + SiO_2 \xrightarrow{373\ K} \longrightarrow (NH_4)_{8-n}SiMo_{11}M^{n+}O_{40}H_2/SiO_2 .$$

† The IR spectra of the Mo_6-HPC of copper and cobalt are identical.
‡ The IR spectra of the Cu and Co salts of Si–Mo- and P–Mo-HPC are similar to those of the corresponding heteropoly acids.

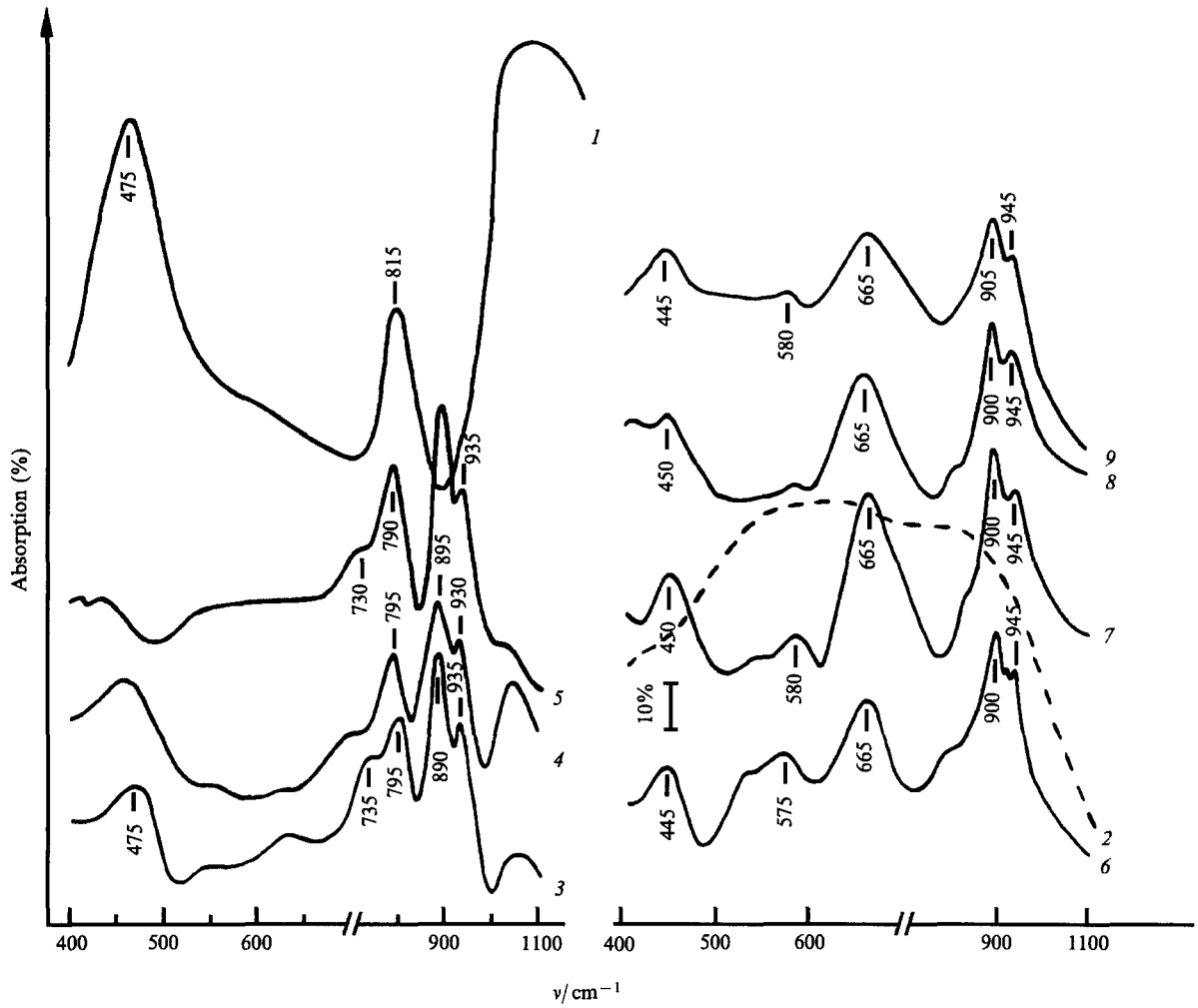


Figure 2. IR spectra of the carriers SiO_2 (*1*) and Al_2O_3 (*2*) and of the samples prepared by supporting Mo_6-HPC on these carriers: *3*) $(NH_4)_4CoMo_6/SiO_2$ (16.5% Mo), *4*) $(NH_4)_4CuMo_6/SiO_2$ (16% Mo), *5*) $(NH_4)_3FeMo_6/SiO_2$ (15% Mo), *6*) $(NH_4)_3AlMo_6/Al_2O_3$ (16.1% Mo), *7*) $(NH_4)_4CuMo_6/Al_2O_3$ (17.6% Mo), *8*) $(NH_4)_4CoMo_6/Al_2O_3$ (16% Mo), *9*) $(NH_4)_3FeMo_6/Al_2O_3$ (16.5% Mo).

When supported on Al_2O_3 the M–Mo_6-HPC (M = Cu, Co, Fe) are converted into Al–Mo_6-HPC with the participation of Al atoms from the carrier surface:

$$(NH_4)_{6-n}M^{n+}Mo_6O_{24}H_6 + Al_2O_3 \xrightarrow{373\ K} \longrightarrow (NH_4)_xM_{(3-x)/n}AlMo_6O_{24}H_6/Al_2O_3 .$$

These processes are of interest from the standpoint of the chemistry of HPC, but they have only very recently begun to be discussed in published work. Results so far available suggest that the tendency of surface atoms to form complexes with molybdenum depends on their nature, and in particular that this property is more clearly developed in Si and Al atoms than in Cu^{2+}, Co^{2+}, and Fe^{3+}. As a result the aluminium and silicon atoms on the carrier surface can displace copper, cobalt, and iron from the central ion position in the mixed HPC.

The IR spectra of Si–Mo_{12}- and P–Mo_{12}-HPC supported on SiO_2 or TiO_2 are identical to the spectra of their copper and cobalt salts on the same supports. The form of the spectra is independent of the content of HPC on the support (5–25 wt.% Mo). In the spectra of P–Mo_{12}-HPA on SiO_2 and TiO_2, we find absorption bands at 790, 875, and 965 cm^{-1} which are also seen in the spectra of massive P–Mo_{12}-HPA (spectrum *2* of Fig. 1). We note that the absorption band at 1065 cm^{-1} seen in the spectra of massive P–Mo-HPC cannot be reliably resolved in the IR spectra of these compounds supported on SiO_2 because of the strong absorption of the carrier in this region (spectrum *1* of Fig. 2). In the spectra of Si–Mo_{12}-HPC supported on SiO_2 and TiO_2 absorption bands can be seen at 780, 865, 910, and 960 cm^{-1}: these are characteristic of the heteropoly anion (HPAn) $SiMo_{12}O_{40}^{4-}$ (spectrum *1* of Fig. 1).

On the whole the good agreement between the IR spectra of bulk P–Mo_{12}- and Si–Mo_{12}-HPA (and their salts) and of the samples supported on SiO_2 and TiO_2 suggests that the structure of the anion of Mo_{12}-HPA is preserved when the material is supported on these carriers.[9,10]

A different state of affairs is found for Mo_{12}-HPC supported on Al_2O_3. The IR spectra of samples prepared by depositing the Cu and Co salts of Si–Mo_{12}-HPA on Al_2O_3 (~15% Mo) are similar. Fig. 3 (spectrum *2*) shows as an example the spectrum of Co_2SiMo_{12}/Al_2O_3, which differs markedly from the characteristic spectrum of the $SiMo_{12}O_{40}^{4-}$ HPA (spectrum *1* of Fig. 1), and is almost identical to the IR spectrum of the NH_4 salt of the Al–Mo-HPA supported on Al_2O_3 (spectrum *6* of Fig. 2). These results indicate the decomposition of $SiMo_{12}O_{40}^{4-}$ when the Cu and Co salts of Si–Mo_{12}-HPA are supported on Al_2O_3 in concentrations of ~15% Mo. Under these conditions Al–Mo_6-HPC are formed on the support. Unlike its salts, the Si–Mo_{12}-HPA itself is preserved when supported on Al_2O_3: the IR spectrum of the Si–Mo_{12}-HPA/Al_2O_3 sample (16.8% Mo) (spectrum *1* of Fig. 3) is similar to that of the massive heteropoly acid (spectrum *1* of Fig. 1).

The IR spectra of the catalysts prepared by supporting the P–Mo-HPA and its Cu and Co salts on Al_2O_3 (concentration of HPC ~15% Mo) are similar (spectra *3* and *4* of Fig. 3), and almost indistinguishable from the spectrum of $(NH_4)_3AlMo_6/Al_2O_3$

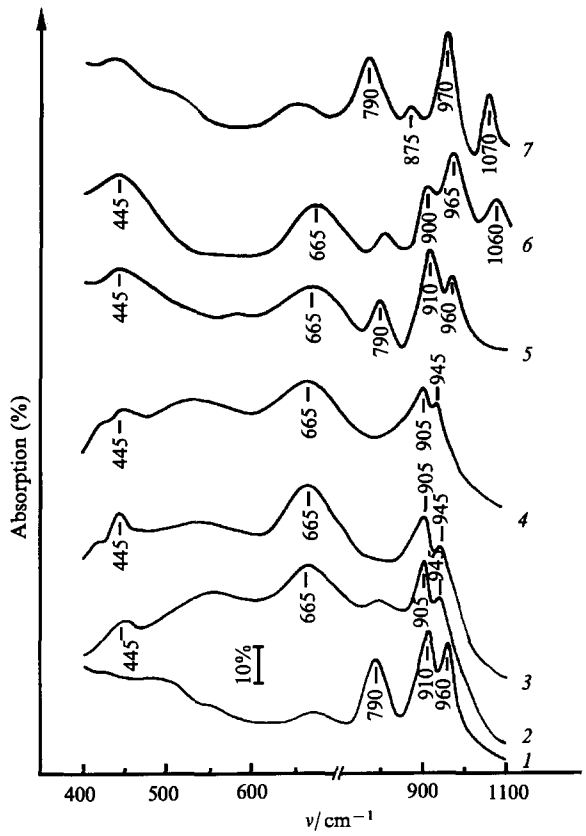


Figure 3. IR spectra of samples prepared by supporting Mo_{12}-HPC on Al_2O_3 and drying at 373 K:
1) H_4SiMo_{12} (16.8% Mo) *2*) Co_2SiMo_{12} (15.5% Mo)
3) $Cu_{3/2}PMo_{12}$ (14.6% Mo) *4*) H_3PMo_{12} (13.3% Mo)
5) Co_2SiMo_{12} (27.3% Mo) *6*) $Co_{3/2}PMo_{12}$ (21.5% Mo)
7) H_3PMo_{12} (23.4% Mo).

(spectrum *6* of Fig. 2). Absorption bands characteristic of the P–Mo_{12}-HPC are not observed in the spectra of these samples.

The totality of these results convincingly shows that at low concentrations (~15% Mo) on the surface of an Al_2O_3 support Mo_{12}-HPC (like Si–Mo_{12}-HPA) is decomposed with formation of Al–Mo_6-HPC by reacting with the aluminium atoms of the Al_2O_3 surface, whereas copper and cobalt cations tend to behave as salt formers:

$$M_xAMo_{12}O_{40} + Al_2O_3 \xrightarrow{373\ K} M_yAlMo_6O_{24}H_6/Al_2O_3 .$$

Fig. 3 also shows the IR spectra of catalysts with large concentrations of Mo_{12}-HPC on Al_2O_3 (23–27 wt.% Mo, spectra *5*–*7*). It can be seen that increasing the concentration of P–Mo_{12}-HPA and its salts (or of the salts of Si–Mo_{12}-HPA) on the support produces, in addition to a weak band at 665 cm^{-1}, characteristic of Al–Mo_6-HPC, absorption bands typical of $SiMo_{12}O_{40}^{4-}$ (780, 860, 910, and 960 cm^{-1}, spectrum *5* of Fig. 3) and of $PMo_{12}O_{40}^{3-}$ (790, 875, 965, and 1065 cm^{-1}, spectra *6* and *7* of Fig. 3). This suggests that at high concentrations the main part of the Mo_{12}-HPC is retained unchanged on the Al_2O_3 surface.

Thus the Mo_{12}-HPC are preserved (irrespectively of their concentration on the surface) when deposited on SiO_2 or TiO_2, whereas on the surface of Al_2O_3 the P–Mo_{12}-HPA and its salts, as well as the salts of Si–Mo_{12}-HPA, decompose at low concentrations with formation of Al–Mo_6-HPC.

These results have been explained[8] in terms of the acid–based properties of the substrates and of the pH stability range of the supported HPC.

As reported,[21,22] the substrates can be arranged in the following order of decreasing acidity: $SiO_2 > TiO_2 > Al_2O_3$. We know that P–Mo-HPA is stable over a very narrow range of pH (0.8–1.5), whereas for Si–Mo-HPA the range is much wider (from 1 to 4).[23,24] Solutions of the Cu and Co salts of Si–Mo- and P–Mo-HPA are also acidic: pH ~2 for $M_{3/2}PMo_{12}$ and pH ~4 for M_2SiMo_{12}.[23] The Mo_6-HPC are stable at higher pH values (2–5.5), and in particular the $AlMo_6O_{24}H_6^{3-}$ anion is preserved up to pH 5.5.[23]

The stability of the structure of Mo_6-HPC when supported on SiO_2 and TiO_2, even at low concentrations of Mo, is probably due to the relatively high acidity of these supports. With a more basic support (such as Al_2O_3) and at low concentrations of Mo_{12}-HPC on the support the heteropoly compound decomposes, lowering the acidity of the medium. As we have shown,[11] under these conditions we observe the formation of Al–Mo_6-HPC, whose anion is stable in less acidic media. At higher concentrations of the HPC on the Al_2O_3 (up to 20–25 wt.% of Mo) the structure of the supported material is retained, probably as a result of the increased acidity of the medium.

Si–Mo-HPA (unlike P–Mo, see above) does not decompose when supported on Al_2O_3, even at low concentrations on the carrier. This is probably due to the wider stability range of Si–Mo-HPA as compared with P–Mo-HPA. On the other hand the salts of the Si–Mo-HPA decompose under these conditions, probably because of the lower acidity of their solutions.

We could therefore have expected that the creation of a strongly acid medium on the surface of samples with a low concentration of HPC on the Al_2O_3 would regenerate the Mo_{12}-HPC after this compound had been decomposed with formation of Al–Mo_6-HPC. To test this hypothesis samples prepared by depositing P–Mo- and Si–Mo-HPC on Al_2O_3 (~15% Mo) were treated with a solution of hydrochloric acid (1 : 1). In the IR spectra of these samples (see Fig. 4, spectra *2*, *4*, and *6*) we found, in contrast to the spectra of the initial catalysts (spectra *1*, *3*, and *5*), absorption bands at 790, 875, 965, and 1065 cm^{-1}, characteristic of P–Mo_{12}-HPA (spectra *2* and *4*) and at 790, 910, and 960 cm^{-1}, characteristic of Si–Mo_{12}-HPA (spectrum *6*), i.e. the increased acidity of the medium induces the reverse conversion of Al–Mo_6-HPC into Si–Mo_{12}- and P–Mo_{12}-HPC.

Thus a study of the interactions of the Mo_6- and Mo_{12}-HPC with the oxide supports leads to the following conclusions. The M–Mo_6 molybdenum heteropoly compounds containing copper, cobalt, or iron as the central atom M are unstable. When supported they interact with the carrier, and as a result mixed Si–Mo–M heteropoly compounds are formed on the SiO_2 surface. On a γ-Al_2O_3 surface the Mo_6-HPC of the transition metals decompose with formation of salts of the Al–Mo_6-HPA. The phase composition of catalysts prepared by depositing Mo_{12}-HPC on supports depends on the acid–base properties of the support and on the pH stability range of the supported HPC. Whereas the structure of P–Mo_{12}- and Si–Mo_{12}-HPC is retained when the compounds are supported on SiO_2 and TiO_2, irrespective of their concentration on the carrier, deposition on Al_2O_3 causes decomposition of the compounds (when present at low concentrations) and the formation of Al–Mo_6-HPC. Thus the composition of the compounds on the surface of basic carriers can be controlled either by varying the concentration of the supported heteropoly compounds or by treating the carriers with solutions of mineral acids.

3. Acidic properties of molybdenum heteropoly compounds

The number of publications dealing with the acidic properties of supported HPC is small. We have described[25] a study of the acidic properties of P–Mo-HPA supported on various oxide carriers (SiO_2, TiO_2, Al_2O_3), and also of Si–Mo-HPA and the salts of P–Mo-HPA on SiO_2. The adsorption of molecules of a base (pyridine[25,26] or ammonia[9]) on these HPC was studied by IR spectroscopy.

It was found that the IR spectra of pyridine adsorbed on any of the HPC in the 1300–1650 cm^{-1} region were similar. The presence of an absorption band at 1540 cm^{-1}, assigned to vibrations in the pyridinium ion, was interpreted[25] as evidence of the presence in all the catalysts of Brønsted-acid centres (BAC)

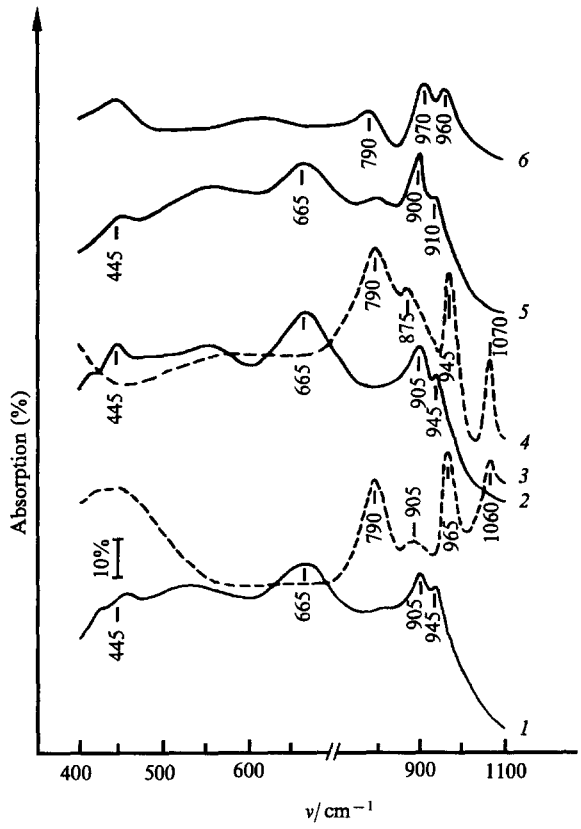


Figure 4. IR spectra of samples prepared by supporting Mo_{12}-HPC on Al_2O_3: *1*) and *2*) H_3PMo_{12} (13.3% Mo), *3*) and *4*) $Co_{3/2}PMo_{12}$ (14.1% Mo), *5*) and *6*) Cu_2SiMo_{12} (16.6% Mo). The spectra *2*, *4*, and *6* were recorded after treating the samples with a solution of HCl.

which protonate the pyridine molecule. The absorption band found at 1450 cm^{-1} denotes the formation of complexes of pyridine with aprotic centres of the catalyst.

Effect of the concentration of HPA. We studied the dependence of the concentration of proton centres (in μmol PyH^+ m^{-2}) on the content of P–Mo- and Si–Mo-HPA on SiO_2 and of P–Mo-HPA on Al_2O_3. All these dependences are of the same type, suggesting that in the region of low concentration of HPA on the carriers (7–15 wt.% of Mo) the amount of BAC increases in proportion to the concentration of HPA. At still higher concentrations of P–Mo- and Si–Mo-HPA on the carrier (up to 20–28 wt.% of Mo) the concentration of mobile protons (in μmol PyH^+ m^{-2}) stays unchanged, but the specific surface decreases.

The increase in the concentration of BAC with increasing content of HPA (in the region of 7–15 wt.% of Mo) was attributed to the increased coverage of the carrier surface by HPA molecules. A further increase in the content of HPA causes agglomeration of the molecules, which lowers the specific surface of the samples while the concentration of the proton centres per m^2 stays constant.

Since according to Okuhara et al.[27] the acidity measured for massive HPA is the bulk value, our results[25] indicate that in the case of supported HPA the main role is played by the surface properties.

The strength of the proton centres (in units of *PA*, or proton affinity[26]) was characterised by the frequency of the stretching vibrations band of the pyridinium ion, which depends on the basic properties of the acidic residue.[25]

The strength of the proton acid centres was unaffected by varying the content of P–Mo- and Si–Mo-HPA on SiO_2 or of P–Mo-HPA on Al_2O_3: the parameter ν^c_{NH} (defined as the position of the centre of gravity of the ν_{NH} band)§ is 2900 cm^{-1} for all the samples of P–Mo- and Si–Mo-HPA on SiO_2, and 2600 cm^{-1} for the HPA supported on Al_2O_3.

The acidic properties of the different HPC were compared at high concentrations of these compounds on the carrier.

Comparing the acidic properties of HPA with P and Si central atoms supported on SiO_2 showed that the concentration of BAC is greater by a factor of 1.4 in H_3PMo_{12}/SiO_2 than in H_4SiMo_{12}/SiO_2 over the whole range of concentrations of the HPA on the carrier. The strength of the proton centres (as previously defined[26]) was the same for P–Mo- and Si–Mo-HPA supported on SiO_2: ν^c_{NH} = 2900 cm^{-1}.

Effect of the type of carrier. It was reported[23] that the concentration of mobile protons in P–Mo-HPA supported on SiO_2 is much higher than in the same compound on Al_2O_3 over a wide range of concentrations of the HPA. The concentration of BAC in P–Mo-HPA supported on TiO_2 (13.7% of Mo) is 0.4 μmol m^{-2}, i.e. three or four times lower than the concentration of BAC in P–Mo-HPA on SiO_2 (13.6% of Mo), for which this quantity is 1.5 μmol m^{-2} (for samples conditioned at the same temperature of 423 K).

By comparing the ν^c_{NH} values obtained for P–Mo-HPA samples on different carriers it was shown that the centres of gravity ν^c_{NH} for HPA/TiO_2 and HPA/Al_2O_3 are strongly shifted towards lower frequencies. Their calculated ν^c_{NH} values were about 2600 cm^{-1}, as compared with 2900 cm^{-1} for HPA/SiO_2. Therefore supporting the P–Mo-HPA on TiO_2 and on Al_2O_3 lowers the strength of the proton centres.

Qualitative results on the change in the number of BAC caused by an increase in the conditioning temperature of Si–Mo-HPA and P–Mo-HPA (and its salts) deposited on SiO_2 were obtained by studying the adsorption of pyridine on these samples. The concentration of mobile protons on all the samples fell when the pretreatment temperature was increased, the effect being most marked following an increase in temperature from 523 to 723 K. The strength of the proton centres (the shift in ν^c_{NH}) was unaffected by increasing the conditioning temperature of the HPC/SiO_2.

Effect of replacing the protons in the HPA by metal cations. This effect was studied[25] for P–Mo-HPA and its sodium and copper salts supported on SiO_2.

Replacing some of the protons in P–Mo-HPA/SiO_2 by Na^+ produces a large change in the proton-donor capacity of the acid centres (as shown by the changes in the contour of ν^c_{NH}). Upon introducing sodium cations the centre of gravity of ν^c_{NH} is shifted towards lower frequencies (the calculated ν^c_{NH} is 2800 cm^{-1} for the salts and 2900 cm^{-1} for the acid). Similar effects were noted in a study[27] of the decrease in the desorption temperature of pyridine from the Na^+ salts of P–W-HPA as compared with its desorption from the acid itself. For the Cu^+ salts of P–Mo-HPA this decrease in the strength of the proton centres was not observed: ν^c_{NH} was the same for H_3PMo_{12}/SiO_2 and $Cu_{3/2}PMo_{12}/SiO_2$.

The change in the concentration of mobile protons caused by the replacement of H^+ by metal cations in P–Mo-HPA showed[25] that for conditioning temperatures between 423 and 723 K the number of BAC (in μmol PyH^+ m^{-2}) decreases monotonically as the concentration of sodium or of copper in the HPC is increased. However, even in the fully substituted salts Na_3PMo_{12}/SiO_2 and $Cu_{3/2}PMo_{12}/SiO_2$ a small number of mobile protons is still detectable.

Lewis-acid centres. As reported[28], the massive HPA and their salts can be classified as proton acids. The concentration of Lewis-acid centres (LAC) in these catalysts is negligibly small (the amplitude of the absorption band due to co-ordinated pyridine is small in comparison with the absorption band of PyH^+).

§ The position of the centre of gravity of the ν_{NH} band of the pyridinium ion was determined from the outline of the ν_{NH} line at 3400–1800 cm^{-1} (see Okuhara et al.[27]).

Studies of the acidic properties of HPC supported on a carrier have shown[9, 25] that the absorption bands which characterise the ions of co-ordinated pyridine and NH_3 are relatively strong. The concentration of LAC in P–Mo-HPA/SiO_2 has been measured, and the dependence of the concentration of LAC on the composition of the HPC and on their heat-treatment temperature was determined.[25]

Thus the results discussed above show that IR spectroscopy can be conveniently used to establish the presence of HPC on carriers (at least, on SiO_2, Al_2O_3, and TiO_2 as carriers). The method can also be used to monitor the formation of similar compounds during the preparation of traditional supported catalysts containing molybdenum. However, it should be noted that in this case the problem is much more complex than the problems considered above. This is due partly to the large number of phases present in the traditional catalysts (as has been repeatedly pointed out in published papers) and partly to the use of very high conditioning temperatures, which cannot fail to cause decomposition of the HPC, even in the case of compounds formed on the carrier surface during the preparation of the catalyst. Nevertheless the possibility of stabilising these compounds by an appropriate choice of support has now been established: in other words, the carrier should be treated as one of the components of the resulting HPC.[9–11]

As was shown by Mastikhin et al.,[29] important information on the changes in acidity of the HPA induced by the support can be obtained by using the PMR method.

III. Supported molybdenum oxide catalysts. Formation, identification, and surface properties of surface compounds

In this section we shall dwell on two aspects of the study of supported molybdenum oxide catalysts: (1) the development of methods of studying supported catalysts, and (2) the analysis of published data on the identification of the compounds formed on the surface of various carriers during their interaction with molybdenum oxide compounds. Of course, equal attention will be paid to the identification of other compounds formed on the surface of the carriers during this interaction. There are recent reports of the formation of HPC on the carrier surface during the deposition of molybdenum and tungsten oxide compounds (including the traditional methods) as a result of the far-reaching interaction of the supported compounds with the carrier.

X-Ray phase analysis is often not suited to the study of oxide systems formed on the surface of carriers, especially when the active component is present at low concentration. In this case IR spectroscopy is the most attractive method, widely used to establish the phase composition of oxide systems including catalysts amorphous to X-rays.[30, 31] To a first approximation the study of supported compounds by IR spectroscopy is similar to the study of adsorbed molecules:[32] in both cases the basic problem is to identify the type of compound formed by the interaction of the supported compound with the surface and to make apparent the changes taking place during this interaction, i.e. in this case IR spectroscopy is used mainly as a method of analytical control, showing the presence of various compounds of interest.¶ This application of IR spectroscopy suffers from the limitations imposed by the use of vibrational spectroscopy in surface chemistry: (1) the inability to provide a complete spectrum of the surface compound, due both to the overlap of the absorption bands of the active component with those of the support, and to the low concentration of the surface compound, and (2) the simultaneous formation on the carrier surface of several compounds and the overlap of the absorption bands belonging to different structures. For supported molybdenum oxide systems these limitations are even more serious because of the need to identify an inorganic surface compound on the surface of an inorganic carrier.

Because of these difficulties spectral compensation methods seem to be the most attractive: they have been reviewed in depth,[14] and are widely used by several workers to establish the nature of the active component,[8–11, 33] including supported molybdenum oxide compounds formed on the surface of carriers.[8–11]

1. Formation and identification of Al–Mo oxide compounds

Aluminium molybdenum oxide catalysts are being intensively studied everywhere because of the extreme importance of hydrodesulphurisation processes in petroleum refining, in which Al–Mo and Al–W systems promoted with cobalt and nickel are the most widely used industrial catalysts. Several reviews[33–36] of the structure and physicochemical properties of Al–Co–Mo hydro-refining catalysts have been published. The study of unpromoted Al–Mo catalysts is also of interest because these materials are active in many hydrocarbon conversion reactions: oxidation, hydrogenation, isomerisation, dehydrogenation, polymerisation, olefin metathesis, and paraffin condensation.

Several methods of preparing Al–Mo catalysts are available: the adsorption of $MoO_2(OH)_2$ on Al_2O_3 from the gas phase,[37] fixing metal-organic complexes on the Al_2O_3 surface,[38, 39] the adsorption of molybdate ions by the carrier from solutions,[40–44] and coprecipitation from solutions of ammonium paramolybdate (APM) and $Al(NO_3)_3$.[45, 46] The simplest and most widely used method relies on impregnation of the formed Al_2O_3 carrier with solutions of ammonium paramolybdate followed by drying and roasting of the catalyst at given temperatures.[37, 47–54]

Depending on the concentration and pH of the APM solution, surface compounds of different composition can be obtained on the carrier.[42, 43, 49–54] This is primarily due to the presence of different associations in the APM solution, depending on the pH and on the concentration.[55, 56] Increasing the pH and lowering the concentration shifts the equilibrium towards the formation of molybdates containing molybdenum ions in a tetrahedral coordination (MoO_4^{2-}). At low pH and high concentrations the dominant species are the isopoly molybdates, in which the molybdenum ions have an octahedral coordination.[50, 54] Furthermore the γ-Al_2O_3 carrier itself has acid–base properties,[22, 50, 54, 57, 58] and therefore an equilibrium determined by the initial pH and concentration of the solution and by the type of carrier is established at the interface with the molybdenum solutions.[42, 43, 50, 54] By using a more acidic carrier (SiO_2) the polymeric compounds can be stabilised at much lower molybdenum concentrations (down to 10%) than on the more basic Al_2O_3. On the strongly basic MgO the formation of octahedral molybdenum polyanions was not detected at any concentration of APM.[54, 59]

The surface OH groups of the carrier can interact with the molybdenum anions with formation of surface compounds. A large decrease (or complete suppression) of the fluorescence background accompanying the Raman spectrum and attributed to the OH groups on the Al_2O_3 surface has been noted[51] after the deposition of APM on the carrier, suggesting a reaction of the APM with the OH groups. A Raman study of Al–Mo catalysts prepared by impregnating Al_2O_3 carriers with APM solutions of pH between 6 and 11 led to the conclusion[50] that at low molybdenum concentrations (1–3 wt.% MoO_3) only MoO_4^{2-} ions are formed on Al_2O_3 even at pH 6, when the impregnating solution contains $Mo_7O_{24}^{6-}$ ions. The dissociation of the $Mo_7O_{24}^{6-}$ ions is attributed[50] to an increase in the pH of the

¶ This does not exclude the use of IR spectroscopy as a structural technique. If the limitations defined below can be overcome the results of IR spectroscopy can be used to establish the structural parameters of the supported compound.

solution due to the increased concentration of OH^- ions in solution produced by the ion-exchange adsorption

$$Al-OH + MoO_4^{2-} \leftrightarrows AlOMoO_3^- + OH^-.$$

The presence of tetrahedral molybdenum ions on the surface of Al–Mo catalysts prepared by adsorption of molybdate ions from dilute solutions APM at a high pH (8.6) has been established.[42, 43] Adsorption from concentrated solutions of APM or at low pH (4.0) results in the stabilisation of octahedral Mo polyanions[42, 43] on the Al_2O_3 surface; these are retained when the sample is dried.

According to Giordano et al.[53] the Al–Mo catalysts (before being heated) contain tetrahedral ions weakly interacting with the OH groups of the Al_2O_3. During the subsequent activation of the catalysts by oxidative high-temperature treatment further interaction of the molybdenum compounds with the carrier surface takes place.

Under these conditions stable monomeric molybdate complexes (MoO_4^{2-}) are formed at low molybdenum concentrations.[52] Experimental confirmation of the formation of a monolayer of tetrahedrally coordinated molybdenum ions has been obtained by different methods, including IR, Raman, and UV spectroscopy, XPS, and others.[37, 50, 52, 53, 60] According to most of the authors at low concentration (5–10 wt.% MoO_3) the whole of the molybdenum in the roasted catalysts is present in a highly dispersed state, and mainly as tetrahedral ions.[52, 53, 61–63] Increasing the concentration of MoO_3 (to 16 wt.%) increases the fraction of the molybdenum in octahedral coordination and forms polymolybdate structures. At even higher molybdenum concentrations the MoO_3 and $Al_2(MoO_4)_3$ phases are formed.[44–46, 50, 52–54, 59, 61, 64]

The degree of crystallinity of the compounds formed in the $MoO_3-Al_2O_3$ system depends on the concentration of molybdenum, and the extent of reaction depends on the heat treatment temperature.[45, 46] An X-ray study of amorphous molybdenum compounds by atomic radial distribution and ESR methods has shown[46] that polymolybdates containing molybdenum in an octahedral coordination are formed, in addition to the MoO_3 and $Al_2(MoO_4)_3$ phases, during the interaction of APM with Al_2O_3. An analysis of aqueous extracts from Al–Mo catalysts led to the same conclusion.[44] According to these results MoO_3 and $Al_2(MoO_4)_3$ are sparingly soluble in water, whereas a large fraction of the supported molybdenum is transferred to the solution when the Al–Mo catalysts are treated with water. The UV spectra of the aqueous extracts suggest the presence of molybdenum isopoly anions. It was therefore concluded[44] that in addition to the MoO_3 and $Al_2(MoO_4)_3$ phases observed by XPA (which are sparingly soluble and cannot pass into the solution) isopoly compounds are also formed on the surface of the Al–Mo catalysts, especially at high molybdenum concentrations. These are apparently responsible for the activity in the hydrogenolysis of thiophen. However, no attempt was made to identify these isopoly compounds directly on the surface of the catalysts.

Shmidt et al.[48] have established the presence in ignited Al–Mo catalysts of three different forms of molybdenum: water-soluble (W), soluble in ammonia (M), and insoluble in either water or ammonia (S). They claim that the water-soluble form is a compound containing molybdenum in an octahedral coordination (and assumed to be active towards the dehydrogenation of cyclohexane), but the nature of this compound was not examined in that study.[48]

In their discussion of the nature of the active centres created on the Al–Mo catalysts and responsible for the oxidation of propene to acetone Giordano et al.[47, 53] assumed that the compounds possessing acidic and oxidising properties and active in the conversion of propene into acetone could be reduced heteropoly acids or compounds of the $Mo_4O_{10}(OH)_2$ type (though the structure and properties of the heteropoly acids were not investigated in that work).

Several studies of the reduction of Al–Mo catalysts have been reported, and some of these have been reviewed in depth.[35, 36] Only a few features of that work call for comment here. The degree of reduction of Al–Mo catalysts increases with the reduction temperature. The reduction of the supported MoO_3 is much less complete than that of the massive compound.[65] It has been shown[53, 66] that the tetrahedral molybdenum ions are more difficult to reduce than the octahedral. On the whole the reduction of Al–Mo catalysts increases the degree of inhomogeneity of the molybdenum because of the different reducibilities of the molybdenum compounds of different composition.[53]

Studies aimed at identifying the molybdenum compounds formed by reduction and at determining their thermal stability and their stability in catalytic reaction[11, 67] have relied mainly on IR spectroscopy.

A special study[11] was made of the sequence of reactions of the molybdenum oxide compounds on the surface of Al_2O_3 during the thermal conditioning of the sample. In particular, in the IR spectrum of the 25% $MoO_3-Al_2O_3$ catalyst dried at 383 K (spectrum *4* of Fig. 5) we find, in addition to the absorption band at 920 cm^{-1}, a group of strong bands at 450, 665, 900, and 945 cm^{-1}, which is characteristic (according to published data) of polymolybdates.[35, 43] The presence of a strong band with a maximum at 945 cm^{-1} indicates the formation of a compound containing molybdenum in an octahedral coordination. By combining these results with those of previous studies by XPA and ESR,[46] and by Raman[50] and by UV and IR spectroscopy,[52] and also with recently formulated propositions,[53, 68] we may conclude that these compounds are polymeric formations consisting of MoO_6 octahedra or heteropoly compounds of molybdenum and aluminium.

In order to identify the resulting polymolybdate we compared[8] the IR spectra of a 25% $MoO_3-Al_2O_3$ catalyst and of ammonium paramolybdate (an isopoly compound), whose molecule consists of seven MoO_6 octahedra (spectrum *8* of Fig. 5), and of the heteropoly Al-Mo compound $(NH_4)_3AlMo_6O_{24}H_6$, whose anion is constructed from six MoO_6 octahedra connected by their edges into a ring (spectrum *9* of Fig. 5).[23, 69–71] In the latter compound the Al atom occupies the central octahedron. As can be seen from Fig. 5 and Table 1 the IR spectroscopic manifestations of the isopoly and the heteropoly compounds are quite different, which allows these compounds to be identified fairly reliably on catalyst surfaces.

By comparing the spectra *4*, *8*, and *9* of Fig. 5 with the spectral data in Table 1 we can see that the spectrum of the 25% $MoO_3-Al_2O_3$ catalyst dried at 383 K is essentially similar to that of the salt of the Al–Mo heteropoly acid: the maxima of the strongest absorption bands in the region of the Mo–O–Mo bridging bonds (445 and 665 cm^{-1}) are in identical positions, and include a triplet in the high-frequency region 880–950 cm^{-1} (Mo=O vibrations).[70] This suggests the formation on the Mo–Al catalyst surface of a compound similar in structure to the Al–Mo-HPA, and disproves the reported[46] formation of an isopoly compound.

It can also be seen from Fig. 5 that the spectrum of the supported HPA salt is more similar to that of the individual salt than is the spectrum of the compound formed on the surface of the 25% $MoO_3-Al_2O_3$ catalyst. This confirms our hypothesis of the effect of the surface aluminium atoms on the spectral characteristics of the heteropoly anion. When the salt of the HPA is deposited on the carrier the heteropoly anion is already formed, whereas during the interaction of ammonium paramolybdate and Al_2O_3 the anion is formed through the participation of aluminium atoms from the carrier surface.

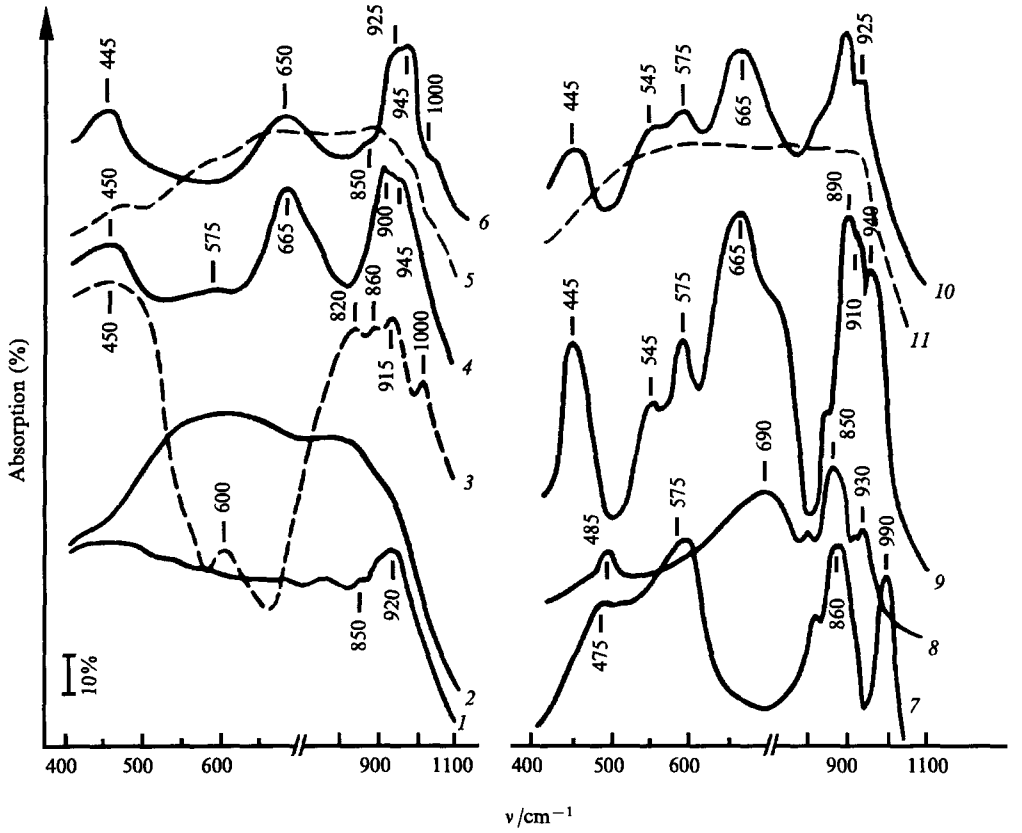


Figure 5. IR spectra of various molybdenum compounds and Mo–Al catalysts: *1*) 10% $MoO_3-Al_2O_3$; *2*) γ-Al_2O_3; *3*) $Al_2(MoO_4)_3$; *4*)–*6*) 25% $MoO_3-Al_2O_3$ at 383 (*4*) and 773 K (*5*), and after treatment with water (*6*); *7*) MoO_3; *8*) $(NH_4)_6Mo_7O_{24}$; *9*) individual $(NH_4)_3AlMo_6O_{24}H_6$; *10*) $(NH_4)_3AlMo_6O_{24}H_6$ supported on Al_2O_3 and dried at 383 K; *11*) ditto, heated at 573 K

In the latter case we can expect the effect of the carrier to be reflected by the IR spectra of the heteropoly anion. Obviously, the same is true of the differences in thermal stability of the heteropoly anions deposited on Al_2O_3 from solutions of their salts or formed by the reaction of ammonium paramolybdate with the carrier. The supported heteropoly compound dissociates even at 573 K (spectrum *11* of Fig. 5), whereas the polymolybdate formations on the surface of the Mo–Al catalysts are not decomposed at 773 K (spectrum *5* of Fig. 5).

Heating the 25% $MoO_3-Al_2O_3$ catalyst to 773 K apparently produces a large perturbation of the octahedral coordination of the molybdenum in the heteropoly compound, which manifests itself in the IR spectrum (spectrum *5* of Fig. 5) as a set of changes in the vibrations of the Mo = O bonds: the absorption band with a maximum at 890 cm^{-1} disappears, and the relative intensities of the bands at 925 and 945 cm^{-1} are increased. However, the character of the spectrum of the catalyst heat treated at 773 K suggests that the polyanion structure of the compound formed during the preparation of the catalyst from ammonium paramolybdate and Al_2O_3 is retained at these quite high temperatures.

Table 1. Position of the absorption bands (cm^{-1}) in the IR of various Mo compounds and Mo–Al catalysts.[14]

$[AlMo_6O_{24}H_6]^{3-}$	$(NH_4)_3[AlMo_6O_{24}H_6]$		Ammonium paramolybdate $(NH_4)_6Mo_7O_{24}$	Aluminium molybdate $Al_2(MoO_4)_3$	MoO_3	25% $MoO_3-Al_2O_3$	
	massive	deposited on Al_2O_3				383 K	773 K
1008 av	–	–	–	1000 av	990 s	–	1000 sh
945 s	945 s	945 s	930 s	–	–	945 s	945 s
922 v.s	910 av	925 av	910 w	915 w	–	920 s	925 s
895 s	890 s	890 s	–	–	–	900 s	–
–	–	–	850 v.w	860 w	860 v.w	–	850 w
–	–	–	–	820 w	820 av	–	–
660 v.s.	660 v.s	665 v.s	690 v.s	600 w	–	665 v.s	665 v.s
572 w	575 av	575 av	–	–	575 v.s	575 w	–
–	545 w	545 w	–	–	–	–	–
483 v.s	–	–	485 av	–	475 s	–	–
467 w	–	–	–	–	–	–	–
445 av	445 av	445 av	–	450 v.s	–	450 av	445 s

Note. Relative intensities of the absorption bands: v.s, very strong; s, strong; av, average; w, weak; v.w, very weak; sh, shoulder.

A comparison of the spectrum of the 25% $MoO_3-Al_2O_3$ catalysts heated at 773 K with the spectra of aluminium molybdate (spectrum *3* of Fig. 5) and of MoO_3 (spectrum *7*) shows that these phases are formed during the heat treatment of the catalyst. The presence of aluminium molybdate is indicated by the higher relative magnitude (as compared with the dried catalyst) of the absorption band at 445 cm^{-1}, and also by the appearance of a band at 920 cm^{-1} (spectrum *3*). The formation of MoO_3 is confirmed by the presence in the spectrum of the heated catalyst of an absorption band at 850 cm^{-1} and a shoulder at 1000 cm^{-1} (spectrum *7*). However, the absorption bands which characterise these phases are relatively weak, i.e. the predominant species on the surface of the heated catalyst are the paramolybdates.

As was pointed out above, one method of establishing the formation of HPC on the surface of carriers is by dissolution, since we know that all the heteropoly acids and many of their salts are readily soluble in water, unlike MoO_3 and aluminium molybdate. It was shown[68] that when these Mo–Al catalysts (with different aluminium contents) are treated with water the amount of molybdenum transferred to the solution is strongly dependent on its concentration in the initial sample. In other words the proportion of water-soluble molybdenum is negligibly small in a 5–10% $MoO_3-Al_2O_3$ sample, but it increases rapidly beyond this point and in a catalyst containing 25% of MoO_3 it amounts to about 50% of the molybdenum added to the sample.

The ^{27}Al NMR spectra of the aqueous extracts indicate the presence of the $AlMo_6O_{24}H_6^{3-}$ anion. It has been shown[11] that, as expected, treating a 25% $MoO_3-Al_2O_3$ catalyst (heated at 773 K) with water, i.e. removing the water-soluble molybdenum from it, produces a marked decrease in the absorption bands which characterise the polymolybdate (spectrum *6* of Fig. 5). This means that the water treatment of the catalyst removes the paramolybdate from the surface of the sample. These results, coupled with the detection of aluminium as well as molybdenum in the aqueous extracts, provide strong additional evidence of the formation of Al–Mo heteropoly compounds on the surface of Mo–Al catalysts with a high molybdenum content.

The presence of polymeric molybdenum compounds in the heat-treated 25% $MoO_3-Al_2O_3$ catalysts is additionally confirmed by the lines at 956, 891, and 345 cm^{-1} seen in the Raman spectra.[72]

Acidic properties. As was pointed out above proton acidity is a special feature of both supported and massive HPC. It should be noted that in order to account for the catalytic properties of Al–Mo catalysts in various reactions[40, 73–76] some workers have postulated the presence of strongly acid centres (including mobile protons) on the surface of these catalysts. Several studies of the acidity of these surfaces have been reported.[75–81] Information on the overall acidity of the catalysts can be obtained from titrations of the molybdenum oxides with *n*-butylamine[76, 77] and from their heats of immersion in pyridine.[75] However, results from different laboratories are usually inconsistent.

According to Parsons and Ternan[76] the acidity of Al–Mo catalysts increases monotonically with the molybdenum content form 2 to 30 wt.% of MoO_3, whereas Ragaini et al.[75] observed a non-monotonic change in the acidity with the content of MoO_3: samples containing 8 and 25 wt.% corresponded to maxima in the acidity. The maximum near 8 wt.% of MoO_3 was attributed[75] to the formation of the protonated $(HMoO_4)^{2-}$ and $(H_2Mo_2O_7)^{2-}$ [or $MoO(OH)^{2+}$] surface structures. At high concentrations (25 wt.% MoO_3) the acidity maximum was interpreted as the formation of $Mo_4O_{10}(OH)_2$ structures,[75] including the Mo^{5+} and Mo^{6+} ions. The decrease in the acidity at low concentrations (up to 4 wt.%) of MoO_3 is explained by the complete neutralisation of the most basic centres in the Al_2O_3 upon the addition of molybdenum. In the catalysts containing more than 27 wt.% of MoO_3 acid centres with H_0 between 6.8 and 3.3 were observed, and in catalysts containing less than 12.5 wt.% of MoO_3 the acid centres had $H_0 < 3.3$ (see Parsons and Ternan[76]).

Spectral studies of the acidity of Al–Mo catalysts by the pyridine adsorption method[78–81] have established the presence of both Lewis and Brønsted acid centres on the surface of these catalysts. The relative concentration of BAC increases with the concentration of molybdenum (from 9 to 25 wt.% of MoO_3),[78] and also when the catalyst is treated with water. Shmidt and coworkers showed[58] that Al–Mo catalysts have two types of BAC, characterised in the IR spectra of adsorbed ammonia by bands at 1450 and 1430 cm^{-1}, the band at the lower frequency being assigned to a compound containing octahedrally coordinated molybdenum ions. Unfortunately the nature of this compound was not established.

We have reported a study[11, 82] aimed at identifying the mutual relationship between the acidity (determined mainly by the BAC) and the formation of postulated molybdenum compounds on the carrier.

In an IR spectroscopic study of the adsorption of ammonia on 25% $MoO_3-Al_2O_3$ catalysts, for which the formation of a heteropoly molybdate had been established, we observed a large number of proton acid centres on the catalyst surface.[82] Kiviat and Petrakis[78] showed that these centres are due to the presence of heteropoly molybdate acidic compounds. Since treating the catalyst with water, which removes the polymolybdate from the surface, greatly lowers the concentration of BAC on the surface of the sample, the proton acidity of the 25% $MoO_3-Al_2O_3$ catalyst can be attributed to the formation of a water-soluble molybdenum compound on the Al_2O_3 surface. As was said above, this acidic compound could be a heteropoly compound of molybdenum and aluminium. The acidic centres (BAC) of these catalysts are relatively strong and can protonate propene, toluene, and ethylene molecules.[82]

Thus an analysis of the extensive published information shows that the formation of various compounds on the Al_2O_3 surface as a result of the deposition of a molybdenum oxide layer is determined by many factors of which the most important are the conditions and the methods used in the preparation of the catalytic system.

The formation on the Al–Mo catalysts of molybdenum ions in the tetrahedral and the octahedral coordination, in relative numbers depending on the composition and on the preparative conditions of the catalysts, is now fairly reliably established. The molybdenum ions in the tetrahedral coordination are present either as isolated MoO_3 units in the monolayer coverage of samples with a low molybdenum content or as aluminium molybdate at high molybdenum concentrations. In samples with a high molybdenum concentration (more than 10 wt.% of Mo) Al–Mo heteropoly compounds are formed on the surface in addition to the MoO_3 phase and to aluminium molybdate: these retain their polyanionic structure up to 773 K as a result of the interaction with the carrier, and are responsible for the strong proton acidity of these catalytic systems.

2. Formation and identification of Si–Mo oxide compounds

We shall assume that the chemical reactions in the Mo/SiO_2 system caused by the deposition of the active component are confined (at least, at low molybdenum concentrations) to the surface, and that bulk phases are not formed.† The state of the molybdenum ions in this system was studied by various methods, (mainly by optical, electronic, and ESR spectroscopy). Most of these studies were aimed at the local suroundings of the molybdenum ions (mainly because of the nature of the chosen methods).

The most important and complex problem seems to be to establish the relationship between the coordination state of the ion

† There are no reports of the formation of silicon molybdates or of solid solutions. The MoO_3 phase is usually observed only for high surface concentrations of molybdenum.

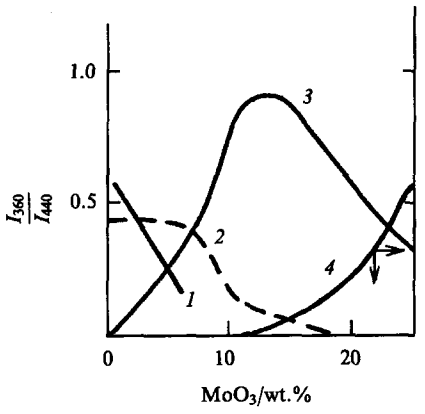


Figure 6. Distribution of the products in MoO_3/SiO_2 as a function of composition, established by titrations of: *1*) dimolybdates (DM), *2*) molybdosilicic acid (MSA), *3*) polymolybdates (PM). The proportion of MoO_3 (in relative units) was determined from the intensity ratio of the IR reflectance bands at 360 and 440 cm^{-1}.

and the type of chemical compound formed on the carrier. XPA is the method traditionally used to solve this problem. However, as in the case of the Mo/Al_2O_3 system, it is applicable only at high concentrations of molybdenum, and therefore vibrational spectroscopy plays an important role[9] in studies of the structure of the molybdenum compounds formed on the surface of SiO_2.

The coordination state of molybdenum at low concentrations was studied by ESR and UV spectroscopy.[83-85] The formation of tetrahedrally and of octahedrally coordinated molybdenum ions was observed. The coordination state of molybdenum was identified from the ESR spectra of Mo^{5+} (used as a paramagnetic probe) on the basis of the correspondence (well established in coordination chemistry) between the structure of the complex and the parameters of the ESR spectra.[86-88] The ESR results agree well with those of diffuse reflectance spectroscopy.[83, 84]

At low molybdenum concentrations tetrahedral molybdenum ions are found on the SiO_2 surface irrespectively of the method of preparing the catalyst. At higher concentrations octahedral molybdenum ions are usually formed as well as tetrahedral ions. However, there also reports of molybdenum ions in the two coordination states in a 1 : 1 ratio at low enough surface concentrations of molybdenum (0.1 Mo atom per 1 nm^2).[85] Whereas the tetrahedrally coordinated molybdenum ions are present as isolated ions in structures of the dimolybdate and MoO_3 type, the nature of the compounds in which the molybdenum is octahedrally coordinated is still problematic.

Castellan et al.[96] studied the Si–Mo system over a wide range of molybdenum concentrations by using a combination of physicochemical methods: XPA, optical spectroscopy, electron microscopy, acidometric titration, etc. From the results they constructed the phase diagram of molybdenum[96] as a function of the molybdenum content of the catalyst (Fig. 6). That work led to the suggestion that the molybdenum is present on the catalyst surface as isopoly and/or heteropoly acids, i.e. that it has a distorted octahedral coordination. In subsequent papers[97, 98] the same workers discussed the catalytic properties of the system towards propene disproportionation and oxidation reactions, and examined a scheme for the formation of products on different active centres.

Mo–Si oxide systems containing between 1 and 20 wt.% of Mo have been studied[9, 88, 89] by ESR and IR spectroscopy. The results were used to correlate the octahedral coordination of molybdenum with the formation of heteropoly compounds. By comparing the results of ESR studies of the state of the molybdenum as a function of the formation temperature of the sample it was concluded[88] that identical changes in the state of the molybdenum take place in the supported Si–Mo-HPA and in the molybdenum oxide catalyst synthesised on the SiO_2 surface (the anisotropic signal denotes stabilisation of the molybdenum in a distorted octahedral coordination of C_{4v} symmetry).

An identification by IR spectroscopy of the types of surface formation on silicon dioxide has been reported.[9] By comparing the IR spectra of SiO_2, MoO_3, and Si–Mo-HPA, and also Si–Mo-HPA supported on SiO_2, it was concluded that the most characteristic absorption bands of these compounds do not overlap (Fig. 7), thus allowing the molybdenum compounds to be identified spectroscopically even at low concentration on the SiO_2 surface. Since the strongest absorption for Mo_{12}-HPA (the Keggin structure) was observed at 700–1100 cm^{-1} and the low-frequency absorption bands are much weaker the absorptions above 700 cm^{-1} were mainly used in the identification of the HPC.

The IR spectrum of the Si–Mo oxide catalyst containing more than 5 wt.% of MoO_3 as the active component, prepared by impregnating SiO_2 with ammonium paramolybdate and drying it at 383 K (spectrum *5* of Fig. 7), was very similar to the spectrum of Si–Mo-HPA supported on SiO_2 (in which the observed absorptions cannot be assigned to ammonium paramolybdate, whose spectrum is also shown in Fig. 7 as spectrum *4*). This suggests the possible formation of Si–Mo-HPA on the SiO_2 surface.[9] Heating this system to 773 K has almost no effect on the form of the spectra (spectrum *6* of Fig. 7), showing that the heteropoly anions are retained on the SiO_2 surface up to quite high temperatures whereas the supported Si–Mo-HPA begins to decompose at 573 K. In the spectrum of the latter sample obtained by compensating for the spectrum of the carrier (spectrum *7* of Fig. 7) weak absorption bands characteristic of trace quantities of the MoO_3 phase are observed in addition to the absorption bands of the HPA. Heating the catalysts at 873 K lowers the intensity of the absorption bands characteristic of HPA and increases that of the MoO_3 bands. After heat treatment at 973 K only the MoO_3 bands can be seen.

Thus an analysis of the spectra of Si–Mo catalysts has shown that the interaction of ammonium paramolybdate with silica produces Si–Mo-HPA, whose thermal stability is higher than that of the heteropoly acid, both individual and supported on SiO_2.[9]

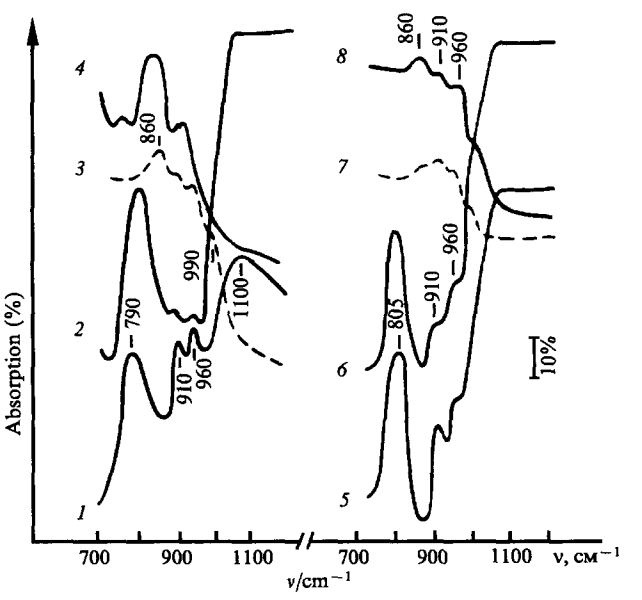


Figure 7. IR spectra of HPA/SiO_2 (spectra *1–3*), ordinary (*1*) and dehydrated at 573 K (*2*) and 673 K (*3*), of ammonium paramolybdate (spectrum *4*) and of a Si–Mo catalyst (spectra *5–8*) dried at 383 K (*5*) and dehydrated at 773 K (*6*, *7*) and 873 K (*8*). The spectra *3*, *7*, and *8* were obtained with compensation of the SiO_2.

Acidic properties. As was pointed out above, a distinguishing feature of the heteropoly acids is their proton acidity. Therefore in order to identify the type of compound formed on the surface of the carrier it is important to establish the nature of the mobile protons.

Studies[9, 91-94] of the acidic properties of Si–Mo oxide catalysts have confirmed the formation of a strong acid.

The IR spectra of ammonia adsorbed on both the HPA/SiO_2 and the Si–Mo catalyst dehydrated at 473 K show the formation of NH_4^+, i.e. the presence of mobile protons on the surface of these samples.[9] Raising the dehydration temperature of the sample from 473 to 573 and 873 K suppresses the intensity of the NH_4^+ absorption bands (as in the case of HPA/SiO_2) by lowering both the number and the strength of the BAC.[9]

The adsorption of ammonia on a Si–Mo catalyst hydrated after being heated to temperatures at which the heteropoly anions are not removed also denotes the presence of BAC. On the other hand after the complete breakdown of the heteropoly acid on the SiO_2 surface after heat treatment at 973 K the ammonium ion is not observed in the spectrum of ammonia adsorbed on the sample rehydrated after decomposition of the polyacid, i.e. in this case the hydration–dehydration processes are irreversible.[9]

Electron defect centres have also been observed on the surface of the Si–Mo system.[95] Thus, the adsorption of aromatic polycyclic hydrocarbon molecules on these catalysts is accompanied by electron transfer from the hydrocarbon to the molybdenum, which forms the corresponding cation radicals and reduces the Mo^{6+} to Mo^{5+}.

It should not be forgotten that an HPA which is thermally stable up to 773 K is formed on the Si–Mo catalysts in addition to MoO_3. This high stability can be attributed to the chemical interaction of the HPA with the carrier (~85–90% of the added molybdenum interacts with the surface according to the chemical analysis results). The thermal stability of this HPA is substantially higher than that of the bulk compound. The presence of mobile protons is associated with the presence of a Si–Mo-HPA on the carrier surface also in this system. The concentration of the protons depends on the degree of hydration of the heteropoly acid.

3. Formation and identification of Ti–Mo compounds

The physicochemical and catalytic properties of Mo/TiO_2 catalysts are largely determined by the method of preparation.[99-102] Catalysts having different phase compositions can be prepared. Thus, in the synthesis of Ti–Mo catalysts by the coprecipitation of molybdenum and titanium oxides, solid solutions based on titanium dioxide are formed. However, the situation is complicated by the formation of two modifications of TiO_2 under these conditions: anatase and rutile.[102, 103] A solid solution of molybdenum oxide in anatase is obtained when ammonium paramolybdate is added to titanium hydroxide paste.[101] The stability of molybdenum is fairly high: up to 25–30 wt.% of MoO_3. The formation of a solid solution is inferred from the abnormally high lattice parameters[104] of the TiO_2 phase, due to the difference in size of Ti^{4+} (r = 0.64 Å), Mo^{6+} (r = 0.66 Å), and Mo^{5+} (r = 0.65 Å). When the Mo–Ti catalyst was prepared by the impregnation of anatase with molybdic acid at low concentrations of Mo only the anatase phase was detected by X-ray diffraction (phases containing Mo could not be detected), and at high concentrations the MoO_3 phase was detected. In the synthesis of a Mo–Ti catalyst from molybdenum tartrate complexes an X-ray amorphous form was obtained.[101]

The effect of the pH used to precipitate the titanium hydroxide on the phase composition of the resulting Mo–Ti catalyst has been studied.[102] However, it was pointed out[89] that the measurements in the region of pH < 1.4 cannot be correct since titanium hydroxide is deposited at pH > 1.4 (see Goroshenko's monograph[103]). A detailed examination[87] of the influence of the method of preparation of the catalyst on the phase composition and on the state of the molybdenum ions showed that the presence of added ions favours the low-temperature formation of rutile and the stabilisation of the molybdenum on the lattice sites and in the interstitial positions of rutile. Molybdenum ions with an octahedral coordination stretched along the tetragonal axis are found in the lattice positions, whereas the interstitial ions are compressed along the same axis. In a catalyst prepared at a high pH without added ions the phase composition was found to depend on the total concentration of added molybdenum.[102]

For molybdenum concentrations up to 25–30 wt.% MoO_3 a solid solution based on TiO_2 is observed by X-ray diffraction. At high molybdenum concentrations MoO_3 is formed in addition to the solid solution. The XPA results were confirmed by IR spectroscopy.[104, 105] It was found that the IR spectrum of the solid solution is almost indistinguishable from the spectrum of titanium dioxide in the region of its characteristic vibrations.

It was also reported[105] that the surface composition of the Ti–Mo oxide catalyst (like that of the Sn–Mo oxide catalyst) differs markedly from the bulk composition by being more enriched in molybdenum. The IR spectrum of this surface layer also differs from the spectrum of the solid solution by the presence of bands characteristic of a compound containing molybdenum. It should be noted that a high proton acidity of the molybdenum compound formed on the surface of the TiO_2 support for concentrations of the active component greater than 5 wt.% of MoO_3 has been reported.[105, 106] This molybdenum compound is the active component (at least, in the oxidation of propene to acetone). However, the compound has not been identified.[105]

By using a combination of different methods (XPA, ESR, and IR spectroscopy) an attempt was made[10] to establish the phase composition of Ti–Mo oxide catalysts prepared by adding ammonium paramolybdate (APM) to a paste of titanium hydroxide and heating the product at 723 K (series A) or by impregnating TiO_2 (anatase) with a solution of APM and heating the product at 723 K (series C). In both cases an anatase phase with lattice parameters identical to those given in the literature was identified by XPA. In the series A catalysts the lattice constants of the anatase increased with the molybdenum content, pointing to the formation of a solid solution. No other phases were observed for Mo concentrations between 1 and 25 wt.% under these conditions. For molybdenum concentrations above 25 wt.% a MoO_3 phase was observed. In the series C catalysts there was no increase in the lattice parameters of anatase when the molybdenum content was increased. Adding 15 wt.% or more of Mo led to the formation of a MoO_3 phase. In this respect the most interesting samples are those of series C containing up to 15 wt.% of Mo, in which phases containing molybdenum are not detected by X-ray diffraction.

A detailed study of the IR and ESR spectral parameters of Ti–Mo oxide systems and of their changes in dehydration–rehydration processes at different temperatures, and a comparison of these spectra with those of Ti–Mo-HPA supported on TiO_2, showed[107, 108] that Ti–Mo-HPA (stable up to 723 K) is formed on the surface during the synthesis of Ti–Mo oxide catalysts. A similar state of affairs exists for the Si–Mo oxide system.

Thus in the Ti–Mo oxide catalysts prepared by adding APM to a paste of titanium hydroxide (series A) several phases are produced, depending on the molybdenum content: a solid solution of molybdenum in TiO_2, Ti–Mo-HPA, and MoO_3. For molybdenum concentrations below 10 wt.% almost the whole of the added molybdenum dissolves in the anatase to give a solid solution. Increasing the concentration of molybdenum in the catalyst results in the formation of new phases on the surface of the solid solution: Ti–Mo-HPA and MoO_3. As the concentration of molybdenum in the catalyst is increased still further the concentration of these phases increases.

In the Ti–Mo catalysts prepared by impregnating anatase with a solution of APM (series C) and heating the sample at 723 K Ti–Mo-HPA is formed for molybdenum concentrations lower

than 15 wt.%, but at higher concentrations MoO_3 is found as well as the HPA. The heteropolymolybdic acid thus obtained has a high thermal stability (up to 723 K).

Acidic properties. The HPA found on the surface of the Ti–Mo oxide catalysts is responsible for their Brønsted acidity.[10] The strong acidity of this type of catalyst and its role in the catalytic reactions have long been recognised,[101, 109–112] even before the formation of a HPA on the catalyst surface had been established.

IV. Thermal stability of molybdenum compounds, decomposition mechanism, role of modifiers

We shall now dwell on two problems directly related to the problems discussed above: the changes induced in the HPC by changes in temperature and the influence of the reaction medium on these changes.

1. Massive and supported heteropoly acids

We shall discuss these problems in terms of the most widely known HPA: molybdophosphoric and molybdosilicic.

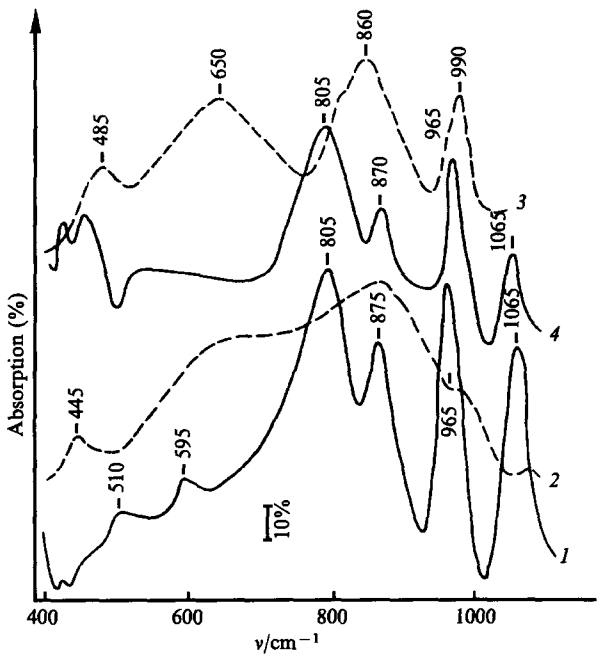


Figure 8. IR spectra of P–Mo-HPA heated at different temperatures: *1*) 673, *2*) 723, *3*) 773 (spectrum *4* relates to hydrated P–Mo-HPA heated at 723 K).

Table 2. Absorption bands in the IR spectra (700–1100 cm^{-1}) of Mo_{12}-HPC (the Keggin structure).

Si–Mo-HPA		P–Mo-HPA		NH_4-salt Ti–Mo-HPA
Ref. 113	Ref. 16	Ref. 113	Ref. 16	Ref. 113
999		1074	1070	1072
960	963	968	972	970
909	915	911		908
859	890	869	882	868
782	782	795	790	790

As was stated above, the IR spectra of Mo_{12}-HPA (the Keggin structure) are typical (Table 2), and those of P–Mo-HPA at 700–1100 cm^{-1} are characterised by strong absorption bands at 805, 875, 965, and 1065 cm^{-1} (Fig. 8). Heating the HPA for 2 h in a stream of air at 673 K does not change the contour of the spectrum, showing that the structure of the Keggin anion is retained. After thermal conditioning of the HPA at 723 K the intensity of the characteristic absorption bands of the HPA decreases rapidly and the shape of the spectrum changes: absorption bands appear at 445 cm^{-1} and in the 700–900 cm^{-1} range, with a maximum at 870 cm^{-1}. Subsequent treatment of the sample with water regenerates the HPA, as shown by the absorption bands at 805, 870, 965, and 1065 cm^{-1} in the spectrum of the hydrated sample (Fig. 8).

According to XPA results the sample heated at 723 K is a mixture of two phases: MoO_3 and a phase with a structure similar to that of Mo_4O_{11}. The MoO_3 phases persists after the treatment with water, but we see a change in the relative intensity of the main diffraction lines on the diffraction pattern of the hydrated sample. The phase with the Mo_4O_{11} structure disappears after the treatment with water.[67]

According to ESR results the state of the molybdenum ions is not markedly affected by heating the sample at 723 K: the molybdenum ions have distorted octahedral surroundings of oxygen atoms, similar to their surroundings in the HPA. In Mo_4O_{11} most of the molybdenum ions also have octahedral surroundings.

In the IR spectrum of the sample heated at 773 K we find absorption bands at 820, 865, and 1000 cm^{-1}, characteristic of MoO_3. After treating the sample with water we find a phase of P–Mo-HPA, and the MoO_3 phase cannot be detected by IR spectroscopy (it can be identified only by XPA).

By comparing the XPA and IR spectroscopy results we reach the following conclusions. After heat treatment of the P–Mo-HPA at temperatures below 623 K the structure of the Keggin anion is retained, whereas heating at 773 K and above causes breakdown of the anion structure and the formation of oxides. In the intermediate temperature region we observe a rearrangement of the Keggin anion with formation of a heteropoly molybdate (poly-oxide) with a structure similar to that of Mo_4O_{11}. We should stress the fact that the similarity between MoO_4 and the poly-oxide (which we shall call a P–Mo-anhydride) lies in their very close structure types, while their chemical natures are quite different. During the hydrolysis the heteropoly molybdate is rearranged into an anion with the Keggin structure, i.e. the process is reversed.

Allowing for these results the process induced by the heat treatment of P–Mo-HPA can be described by the scheme

$$\text{HPA} \leftrightarrows \text{P–Mo-anhydride} \rightarrow MoO_3 + P_2O_5 .$$

It follows from these results that in the region of 723 K the treatment with water produces a reversible rearrangement of the heteropoly anion into a phosphorus–molybdenum anhydride with a structure of the Mo_4O_{11} type. At 773 K this P–Mo-anhydride (poly-oxide) decomposes with formation of MoO_3. The dissociation of the heteropoly anion with an intermediate formation of a compound having the Mo_4O_{11} structure has been reported[18] for several HPA and their salts. It is interesting to note that the addition of water to the anhydride produces the HPA, whence it follows that the poly-oxide is a dehydration product of the HPA, and also that the coordination of the molybdenum ion is not significantly changed in the transition from the heteropoly anion to the poly-oxide: the distorted octahedral coordination is retained. As a result the reducibility of the molybdenum ions is the same in the HPA and in the poly-oxide.

The reduction temperatures of the Mo^{6+} ions to Mo^{5+} by hydrogen (with the corresponding temperatures for the reduction by atomic hydrogen shown in brackets) are listed below for some HPA, for phosphorus–molybdenum poly-oxide, and (for comparison) for MoO_3.

System	T/K
Si–Mo-HPA/SiO_2	373 (300)
Si–Mo-HPA	373 (300)
P–Mo-HPA	373–423
MoO_3	623

As can be seen, the poly-compounds are reduced at the same temperatures, which are much lower than the reduction temperature of MoO_3.

Similar results have been reported for supported systems.[67]

A study by IR spectroscopy and XPA of the change in phase composition as a function of the heating temperature of the P–Mo-HPA supported on SiO_2 showed that after being conditioned at 673 K the sample consists of a mixture of phases: HPA (the principal phase) and anhydride. Increasing the heating temperature to 723 K increases the content of heteropoly molybdate in the sample, and also produces a phase of molybdenum oxide. Therefore the rearrangement of the Keggin anion continues at 723 K. As in the case of massive HPA the heteropoly molybdate phase disappears during the subsequent hydrolysis, and the MoO_3 phase undergoes changes probably due to its texturing by the action of the water. After heat treatment at 773 K the structure of the anion is completely broken down (according to XPA results), and molybdenum oxide is formed: in other words we observe (on the whole) the same stages in the thermal dehydration of P–Mo-HPA supported on SiO_2 as in the dehydration of the massive HPA.

An analysis of the changes in the spectra of supported Si–Mo-HPA during heat treatment shows that above 673 K (or 573 K for the massive HPA) the compound dissociates with formation of MoO_3, as indicated by the appearance of new absorption bands at 860 cm^{-1} ($\nu_{Mo-O-Mo}$) and 990 cm^{-1} ($\nu_{Mo=O}$), which are the most characteristic lines in the MoO_3 spectrum, whereas the appearance of absorption bands in the region of 1100 cm^{-1} denotes the presence of SiO_2 (spectrum *2* of Fig. 7).[29] The complete decomposition of the supported Si–Mo-HPA with formation of MoO_3 and SiO_2 is observed at 773 K: in this case the IR spectrum is a superposition of the spectra of the individual MoO_3 and SiO_2. Thus, in spite of the fact that the deposition of the Si–Mo-HPA increases its thermal stability in comparison with the massive HPA, the nature of the transformations during the thermal conditioning is unchanged.

It should be noted that it has not yet been possible in this case to identify the intermediate compound (anhydride) from the IR spectra (the difficulty being even greater for the Si–Mo oxide catalysts) because of the low intensity of the characteristic absorption bands.[114] However, as in the case discussed above for P–Mo-HPA the spectral changes caused by hydration are reversible up to a dehydration temperature of 773 K for the Si–Mo oxide systems.

Modified catalysts. As has already been pointed out, modifiers are often added to complex catalysts containing molybdenum: for example, phosphorus (in the form of orthophosphoric acid).[115–117] The modifier alters the catalytic properties of the system. However, the role of the phosphorus is still unclear in most cases. There are reports of the formation of surface phases containing phosphorus and molybdenum during the modification by phosphorus,[115–118] i.e. the effect of phosphorus additions can be attributed to chemical changes leading to the formation of P–Mo-HPA and its salts, since the addition of orthophosphoric acid provides an element capable of acting as hetero-atom as well as lowering the pH of the medium.

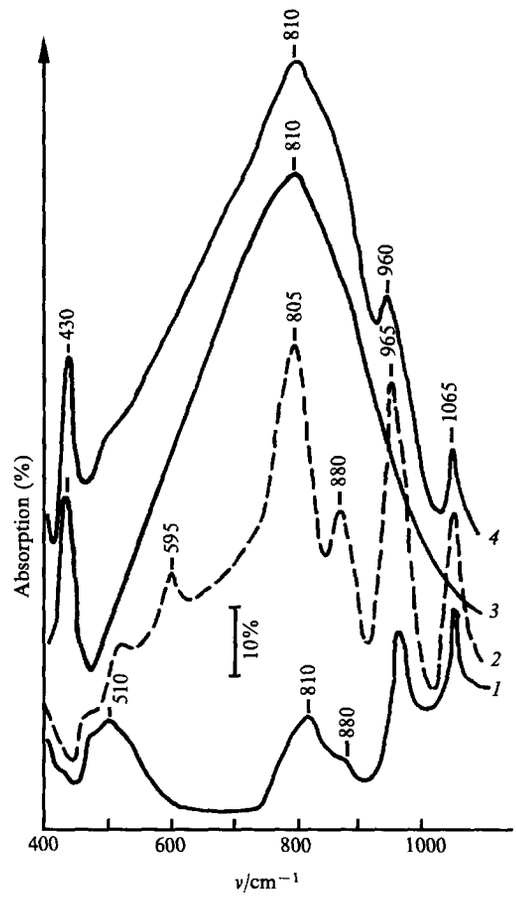


Figure 9. IR spectra of P–Mo-HPA (*1*), $CaMoO_4$ (*2*), and P–Mo-HPA supported on $CaMoO_4$ (*3* and *4*). For comparison we show the spectrum of P–Mo-HPA supported on $CaMoO_4$ taken with compensation for the molybdate absorption.

The possibility of forming P–Mo-HPA by modifying calcium molybdate with orthophosphoric acid has been investigated.[67] Bands at 800–900 cm^{-1}, characteristic of the HPA, were not seen in the IR spectrum of P–Mo-HPA supported on $CaMoO_4$, measured on a background of molybdate absorption (Fig. 9). Only the absorption bands at 960 and 1065 cm^{-1}, characteristic of the Mo = O vibrations and of the vibrations of the central PO_4 tetrahedron in the HPA anion respectively, are clearly seen (spectrum *4* of Fig. 9). The spectrum of supported HPA (with compensation for the absorption of the carrier) is indistinguishable from that of the massive HPA (spectrum *1* of Fig. 9), i.e. these results show that the P–Mo-HPA on the surface of $CaMoO_4$ can be identified reliably from the IR spectra.

The introduction of a superstoichiometric amount of molybdenum into $CaMoO_4$ by treating it with a solution of ammonium paramolybdate and heating the product at 773 K leads to the formation of a MoO_3 phase (Fig. 10). In this case, in addition to an absorption band at 430 cm^{-1} and a strong absorption in the 600–860 cm^{-1} region, characteristic of the molybdate, we find absorption bands at 475, 610, 820, 860, and 995 cm^{-1}, characteristic of molybdenum oxide (spectrum *2* of Fig. 10). By using the compensation procedure we can generate a spectrum for $CaMoO_4$ exactly similar to the initial spectrum, thus confirming that the symmetry of the molybdenum in $CaMoO_4$ is not affected by the addition of a superstoichiometric amount of MoO_3, i.e. indicating the formation of an individual phase of MoO_3. A similar effect has been observed in magnesium molybdate containing superstoichiometric MoO_3.[119]

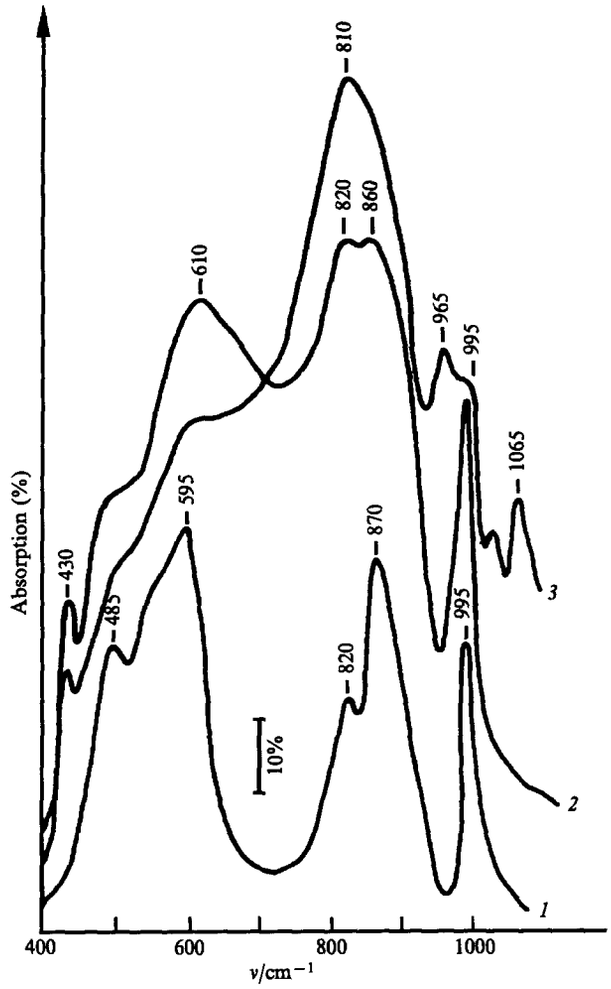


Figure 10. IR spectra of MoO_3 (*1*) and of $CaMoO_4$ modified by 10 wt.% of molybdenum (*2*); *3*) is the spectrum of the same sample after the addition of phosphorus.

Treating a $CaMoO_4-MoO_3$ catalyst with a solution of orthophosphoric acid produces substantial changes in the IR spectrum. The MoO_3 absorption band becomes weaker, and new absorption bands appear at 965 and 1065 cm^{-1} (spectrum *3* of Fig. 10). As was pointed out above, these bands are characteristic of P–Mo-HPA supported on molybdate.

Heating the catalyst at 623 K does not change the shape of the spectrum, confirming that the HPA is stable at this temperature. The absorption bands of the HPA are completely suppressed (i.e. the anion structure is broken down) only after heat treatment of the catalyst at 673 K.

Thus the modification of calcium molybdate with a super-stoichiometric molybdenum content by treatment with phosphoric acid produces a P–Mo heteropoly acid stable up to 623 K.

V. Conclusions

The review of published data has shown that vibrational spectroscopy methods, now widely used in studies of the molecular structure of heteropoly compounds, can also be used successfully to identify these compounds when supported on carriers and when forming compounds on the carriers during the preparation of supported catalysts containing molybdenum and tungsten. We have not dwelt in detail on the interpretation of the spectra of HPC because this topic is already adequately reviewed.[13, 15–17, 24] However, it should be noted that in complex molecules a complete analysis of the normal vibrations is too laborious, and the absorption bands are usually assigned in the approximation of group vibrations.[16]

In the Keggin heteropoly anion we identify groups of atoms whose vibrations are not significantly influenced by the vibrations of the other atoms: 12 terminal Mo=O double bonds, 12 almost linear and 12 bridging Mo–O–Mo bonds, and 12 simple M–O bonds in which the oxygen atoms are shared by three molybdenum atoms and by the central hetero-atom.

It is generally accepted[16, 17] that the stretching vibrations of the bridging Mo–O–Mo bonds are observed in the 900–800 cm^{-1} region, and the vibrations of the Mo–O bonds below 600 cm^{-1}. Bands below 300 cm^{-1} are assigned to bending vibrations of the anion skeleton. The vibrations of the central tetrahedron appear at 1100–800 and at 600 cm^{-1}. The vibrations of the Mo=O bond appear at 900–1000 cm^{-1}.

The IR spectra of the Mo_{12}-HPA (the Keggin structure) are characteristic and can be used to identify the molecular structure of the heteropoly compounds.

We have shown that the Mo_6-HPC, in which the central atoms are transition metal ions (copper, cobalt, iron), are unstable. Strong chemical interactions with the carrier take place when these compounds are supported.

The observed influence of the acid–base properties of the carrier on the rearrangement of the heteropoly anion when supported is of great importance. On SiO_2 the Mo_6-HPA are converted into mixed Si–Mo_{12}–M-HPC, in whose coordination sphere the transition-metal cations replace the molybdenum ions. When supported on aluminium oxide the copper, cobalt, and iron heteropoly molybdates are converted into aluminium compounds (by reacting with the surface ions of the carrier).

The Mo_{12}-HPC are stable on SiO_2 and TiO_2 surfaces, but on Al_2O_3 they decompose (when at low concentrations) and they form Al–Mo_6-HPC at high concentrations.

This detailed review of the processes taking place on the surface of TiO_2, SiO_2, Al_2O_3 carriers during the formation of supported molybdenum catalysts has demonstrated the possibility of using vibrational spectroscopy in the identification of the compounds formed on the carrier surface and in establishing their origin.

Spectral criteria for the identification of HPC on carriers (even with inadequate spectral information) have been formulated, and they can be used to obtain reliable information on the resulting compounds. It was established that far-reaching interactions between the active component and the carrier usually take place, leading to the formation of new compounds. We have also examined the formation of different types of HPC on the carrier surface, depending on the acid–base properties of the carrier.

A detailed comparative analysis of published data on the occurrence of acidic properties (at least for the case of proton acidity) in these catalysts and supported HPC has shown that strong proton acidity is a necessary criterion for the formation of HPC on carrier surfaces during the preparation of catalysts.

Extensive evidence is now available of the important role of surface centres of this type (and of the role of the HPC formed on the surface of carriers) in catalytic processes.[3, 54, 67, 89, 106, 110, 120–124] It has been reported[67] that at least in some processes (for example, in the oxidation of propene and of methanol) the HPC are retained on the surface after its interaction with the reaction medium at the temperature and other conditions of the catalytic reaction.

The study of the decomposition of massive and of supported HPA has revealed the formation of acid anhydrides during their dehydration, and their reversible conversion into the initial HPC by hydration.

The possibility of forming HPC on the surface of molybdates with a superstoichiometric molybdenum content during their modification with acids (for example, phosphoric) has been demonstrated.

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