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A THERMOANALYTIC–MASS SPECTROMETRIC STUDY OF OXIDE-SUPPORTED ACETYL ACETONATES

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ABSTRACT

The present DTA/MS study concerns M(acac)$_n$/support materials, in which M = Pd^{2+}, Pt^{2+}, MoO_2^{2+}, Fe^{3+}, Ru^{3+} or Ni^{2+}, and support = SiO_2, γ-Al_2O_3 or TiO_2. The thermal behaviour depends, in the first place, on whether the complex is chemisorbed, i.e. has reacted in the adsorption step, or is simply physisorbed. Then, there is the influence of M, even in the case of M(acac)$_n$ chemisorbed on γ-Al_2O_3, where the acac is no longer associated with M, but with the surface Al ions. Lastly, the support also plays a role, and it is only with SiO_2 that the simplest decomposition reaction, H transfer from surface OH groups to adsorbed M(acac)$_n$ to form acacH, is consistently observed.

INTRODUCTION

Over the past few years, this group has been studying the interaction of transition metal acetylacetonates (2,4-pentanedionates) with oxidic surfaces in order to ascertain whether these complexes can be fruitfully applied in catalyst preparation and whether they could be used to effectively titrate specific oxide surface sites [1]. The approach taken was to adsorb the acetylacetonate onto the oxide from a solution of the complex in an organic solvent and then to analyse the adsorption solution and to try and characterize the structure of the adsorbate using mainly FTIR spectroscopy. However, one would also like to know the stoichiometry of the adsorbed phase, i.e. the number of acac ligands (acacH = acetylacetone) remaining, and thermogravimetry coupled with mass spectrometry would appear to be ideally suited for this purpose. It turned out that acac decomposition depends on the transition metal as well as on the oxide support. Because acetylacetonates are often used to prepare oxide layers on an (oxidic) substrate, this discovery should be of more general interest, and the pertinent results are reported here.

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EXPERIMENTAL

Samples were prepared using controlled adsorption as previously described [1]. In some cases, where no adsorption was observed to occur, samples were prepared using "wet" impregnation, the solvent being removed in a rotary evaporator under reduced pressure. The oxide carriers employed were γ-Al_2O_3, SCS 79 (95 $m^2\ g^{-1}$) and CK 300 (190 $m^2\ g^{-1}$), SiO_2 (265 $m^2\ g^{-1}$) and TiO_2, P25 ex-Degussa (50 $m^2\ g^{-1}$).

The DSC/TG experiments were carried out on a Mettler TA 2000 system in a N_2 or Ar flow (30 ml min^{-1}). The DSC results varied with O_2 impurity level, as will be described at the end of the paper. Generally, N_2 containing 10–20 ppm O_2 was used. Mass spectra were obtained in a separate experiment with a MAT 731 mass spectrometer. Samples were introduced into the ion source via a direct introduction probe which could be heated to around 450 ° C. In general, the position of the maxima in DTG (DSC) and the mass fragmentogrammes did not differ much ($\pm 20\,°$C), so that desorption product identification was possible and relatively straightforward.

RESULTS AND DISCUSSION

SiO_2

Most of the acac complexes employed in this study failed to adsorb on SiO_2. Samples of silica-supported $Pd(acac)_2$ and $Pt(acac)_2$ were prepared using impregnation (solvent, benzene). With heating, a single process was observed, characterized by a sharp exotherm, (compare Fig. 1, dotted curve). AcacH was the only desorption product and the weight loss corresponds, within experimental error, to the amount of acac introduced. It seems, therefore, that this is a simple, well-defined reaction between silica surface hydroxyl groups and the acac complex

$$n\mathrm{OH_s} + \mathrm{M(acac)}_n \rightarrow (\mathrm{O_s})_n\mathrm{M} + n\,\mathrm{acacH} \qquad (1)$$

where the subscript s denotes surface species.

A sample of $MoO_2(acac)_2/SiO_2$ was also prepared using impregnation (solvent, methanol (MeOH)). The decomposition process was somewhat more complicated than in the previous case. The DSC signal is shown in Fig. 2, curve a. The total weight loss is slightly less ($\sim$ 10%) than the amount of acac present in the sample, and it occurs in three distinct steps. The first 40% is lost between 120 and 200 ° C, the sole desorption product being acacH; it is striking that no heat effect is associated with this process. The next 40% of the weight loss is associated with the first exotherm and corresponds to the formation of, again, acacH (compare Fig. 2, curve b), acetone and, presumably, acetovanillone ($C_9H_{10}O_3$, $m/z = 166$, 151, 123),

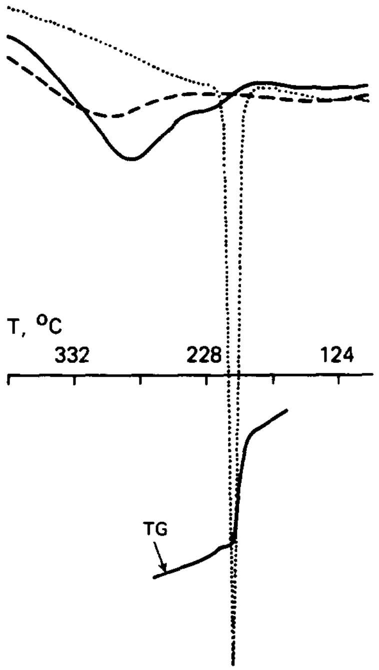
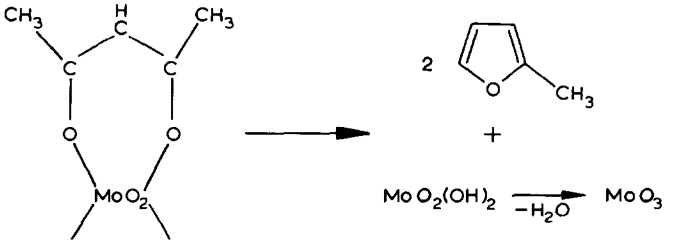


Fig. 1. DSC signals of some $Pt(acac)_2$ samples: ······, $Pt(acac)_2/SiO_2$ (0.89% Pt), TG also shown: – – –, $Pt(acac)_2/\gamma\text{-}Al_2O_3$ (0.65% Pt); ———, $Pt(acac)_2/\gamma\text{-}Al_2O_3$ (1.5% Pt). ($\gamma\text{-}Al_2O_3$ = CK 300).

which needs the condensation of two acac species for its formation. The last 20% is lost during the second exotherm. Here the main product is methylfuran and minor peaks are also observed at $m/z = 65, 77, 79, 91, 105, 107, 121$ and 122, which would indicate the presence of dimethylphenols and methylanisoles. Methylfuran can readily be envisaged as being formed from $MoO_2(acac)_2$ through ring closure and "internal" H_2O abstraction



(2)

In this case, then, eqn. (1) accounts for only part of the complex decomposition, the complex persisting to higher temperatures where the decomposition is apparently dominated by intramolecular reactions, rather than a reaction between it and the support.

Although $Fe(acac)_3$ does not adsorb on SiO_2 from MeOH solution, it does adsorb from toluene. Physisorption accounts for about half the amount

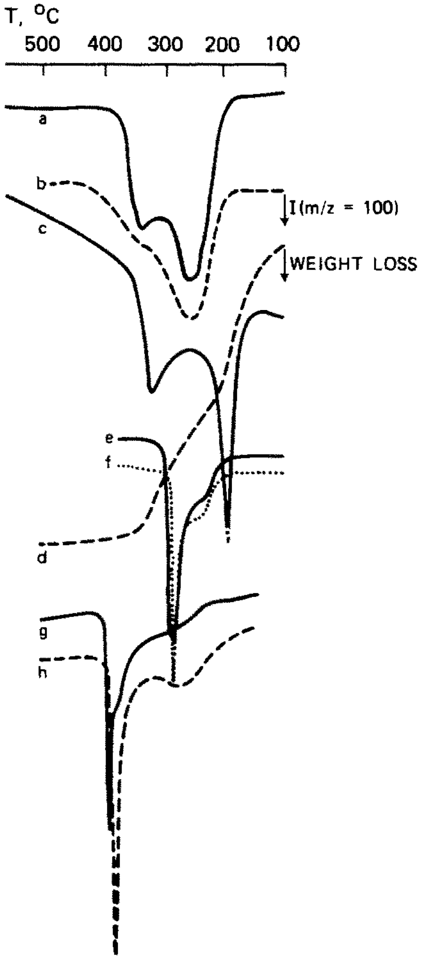


Fig. 2. Summary of results for SiO_2-supported complexes: a, DSC, $MoO_2(acac)_2$; b, acacH generation, $MoO_2(acac)_2$; c, DSC, $Fe(acac)_3$; d, TG, $Fe(acac)_3$; e, DSC, $Ru(acac)_3$ adsorbed; f, DSC, $Ru(acac)_3$, impregnated; g, DSC, $Ni(acac)_2 \cdot 2H_2O$, $t(ads) = 1$ month; h, DSC, $Ni(acac)_2 \cdot 2H_2O$, $t(ads) = 4$ h.

of $Fe(acac)_3$ adsorbed (this fraction can afterwards be desorbed in MeOH). The rest is fixed on the silica via a reaction with the surface hydroxyl groups with the concomitant formation of acacH. Determination of the concentration of the latter in the toluene phase by GLC demonstrated that roughly two acac ligands are lost per Fe adsorbed

$$2OH_s + Fe(acac)_3 \rightarrow (O_s)_2Fe(acac) + 2acacH \qquad (3)$$

Decomposition of the adsorbed phase is a two-step process (see Fig. 2, curve c). The first exotherm is due to the physisorbed molecules, which, as acacH is the sole desorbate, react according to eqn. (1). The second exotherm is due to the Fe(acac) surface species, and MS detected a single product, acetone. It is not clear what happened to the remainder of the acac ligands: IR showed that no carbonyl or carboxyl-containing species remained on the surface, while the colour of the ex-DTA(MS) sample, slightly greyish red, indicated that only very little carbonaceous residue was formed. The TG curve shows that the two decomposition processes are not well-separated (Fig. 2, curve d), which was confirmed by MS, which showed considerable tailing of the acacH desorption curve. The total weight loss was that expected for 50% physisorption and 50% anchoring via eqn. (3).

Unsupported $Fe(acac)_3$ has been variously reported to only volatilize [2] or to decompose with formation of, among other products, methane and acetaldehyde [3]. As is clear from the above, SiO_2-supported $Fe(acac)_3$ behaves in a completely different way; this is due not only to the complex being highly dispersed, but also to the silica hydroxyl groups being involved in the disintegration reaction.

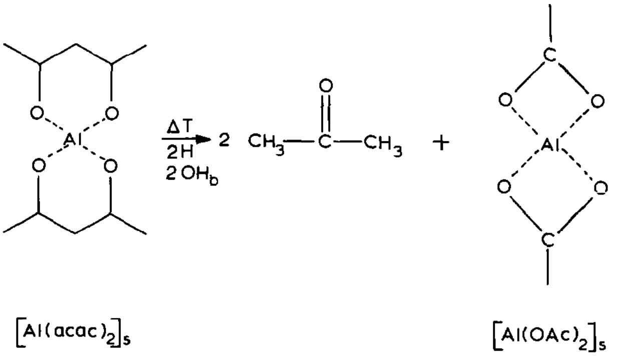
From toluene solution, $Ru(acac)_3$ adsorbs on SiO_2 in essentially the same ways as $Fe(acac)_3$, although the level of adsorption is lower and the fraction of physisorbed molecules greater (70%). The sorption reaction (3) is slow for Ru, and a virtually $[Ru(acac)]_2$-free sample can be prepared using impregnation. From Fig. 2, curves e and f, it is evident that the surface species decomposes at only a very slightly higher temperature than the physisorbed species. In both cases, however, the product is acacH, no acetone at all being observed for the sample containing the Ru(acac) surface species, in contrast to what was found with its Fe counterpart (see above).

It has been proposed in the literature [4,5] that a simple proton transfer from a surface hydroxyl group to the acac ligands governs the acac–complex adsorption process for all oxides. This is not true [1]. As far as chemisorption on SiO_2 is concerned, however, the proposed mechanism, eqns. (1) and (3), does in fact obtain and even describes the behaviour upon heating of physisorbed $M(acac)_n$ on SiO_2 in the majority of cases, $MoO_2(acac)_2$ being a (partial) exception.

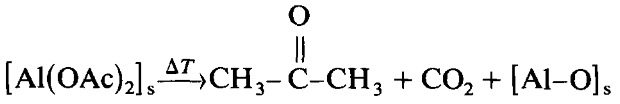
γ-Al_2O_3

The interaction of acacH with γ-Al_2O_3 leads to the formation of $Al(acac)_3$ and an $Al(acac)_x$ surface species, where x is probably two [1]. If benzene is used as the solvent, $Al(acac)_3$ remains in the catalyst surface. Upon heating, it is desorbed at around 190 °C without any detectable heat effect. Mass spectrometry did not detect the $Al(acac)_3^+$ molecular ion, however, but $Al(acac)_2^+$ ($m/z = 225$, observed isotope pattern agrees with the calculated one) and $acacH^+$. Apparently, then, $Al(acac)_3$ does not simply volatilize, as reported for the unsupported complex [2], but abstracts an H atom (from H_2O or a surface hydroxyl group) with formation of the two species mentioned above.

A sample containing only $[Al(acac)_x]_s$ showed, upon heating, two weak exotherms, at ~ 300 and ~ 500 °C, Fig. 3, curve a, with the weight loss being mainly associated with the second one. At 300 °C, a little acetone is formed, and at 500 °C there is a variety of products, including, again, acetone, and CO_2. An IR spectrum, taken after heating for 3/4 h at 525 °C in vacuo, indicated (1) that no acac remains on the surface, but that some carboxylic species are still present, and (ii) that hydroxyl groups, preferentially the basic ones [6], are involved in the disintegration of the surface acac species. The following scheme can be proposed



(4)



$$[Al(OAc)_2]_s \xrightarrow{\Delta T} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + CO_2 + [Al-O]_s \qquad (5)$$

where OH_b denotes basic OH groups (in the final state the O of $[Al-O]_s$ will not remain singly bonded, but will be shared between the Al of the original acac complex and one or both of the Al that have lost a hydroxyl group). In the sample under discussion, reaction (4) occurred only to a minor extent at around 300 °C, and reaction (5) was not complete at 525 °C. The scheme is somewhat simplified in that at high temperatures, (low intensity) peaks at $m/z = 71$, 105 and 120, possibly deriving from aromatic compounds, were also detected. However, because the sample following the MS experiment was white, no carbonaceous residue remains on the catalyst surface.

Most acac complexes chemisorb on γ-Al_2O_3 via a reaction with coordinatively unsaturated (c.u.s.) Al^{3+} sites in the alumina surface, always leading to the $[Al(acac)_x]_s$ species [1]. Its decomposition pattern is not, in the first instance, influenced in the $MoO_2(acac)_2/Al_2O_3$ samples by the Mo present: it is only at high loadings, where the complex also chemisorbs with removal of basic OH groups [1,6b], that the 500 °C process appears to follow a somewhat different path: more aromatic compounds are formed, some of which remain on the catalyst surface, giving the sample a brown colour.

With $Fe(acac)_3/Al_2O_3$, in contrast, Fe catalyses the decomposition of the $Al(acac)_x$ surface species, leading to a single exotherm near 340 °C, Fig. 3,

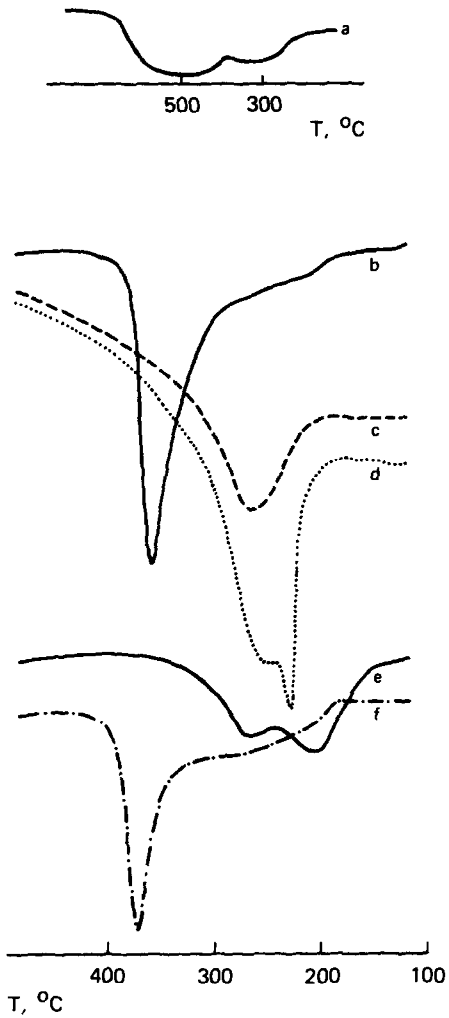


Fig. 3. DSC signals of Al_2O_3-supported complexes: a, acacH; b, $Fe(acac)_3$; c, $Pd(acac)_2$, *chemisorbed; d,* $Pd(acac)_2$, *chemi- and physisorbed; e,* $Ru(acac)_3$; f, $Ni(acac)_2 \cdot 2H_2O$.

curve b, with which the total weight loss is associated. Only acetone leaves the surface; no CO_2 was detected.

Similar results were obtained with $Pd(acac)_2/Al_2O_3$, with the exotherm now occuring at 250–260 °C, Fig. 3 curve c. Comparing the IR spectra of heat-treated acacH/Al_2O_3 and $Pd(acac)_2/Al_2O_3$, Fig. 4, it appears that in the latter, apart from the doublet at 1580 and 1480 cm^{-1} due to the carboxylate species *, another band is present at 1520 cm^{-1}, which may be

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* These bands are not due to (a) surface carbonate(s), because these are known to be unstable on pure alumina [7].

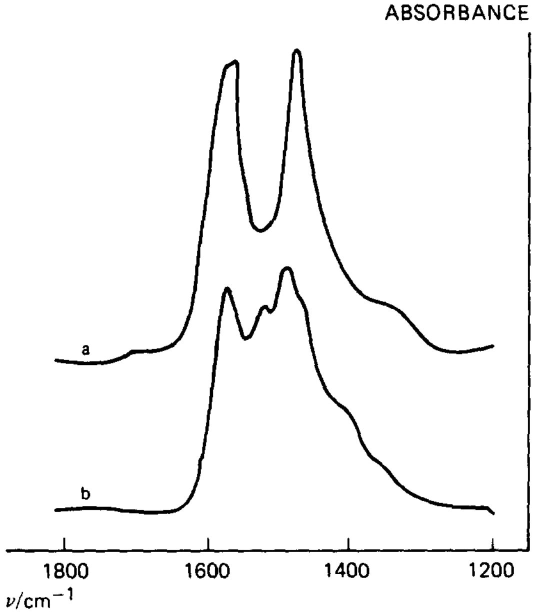

Fig. 4. IR spectra of: a, acacH/Al_2O_3; and b, $Pd(acac)_2/Al_2O_3$, taken after heating 3/4 h at 525 °C in vacuo.

due to the carbonate, formed in reaction (5), remaining adsorbed, instead of forming CO_2 and $[Al-O]_s$, because of the presence of Pd^{2+} (or Fe^{3+}). After $Pd(acac)_2$ chemisorption has been completed, its physisorption can occur. In DTA, Fig. 3, curve d, the decomposition of the physisorbed complex is well separated from that of its chemisorbed counterpart. In fact, a sharp exotherm is observed at 220 °C, reminiscent of the $Pd(acac)_2/SiO_2$ system: a further instance of eqn. (1), therefore (no acacH was seen in MS, but this may be due to the fact that acacH interacts strongly with γ-Al_2O_3, so that it may not escape). This is the only instance of a simple H transfer occurring between a surface OH and the acac ligands in the Al_2O_3-supported systems studied here.

Although the interaction of $Pt(acac)_2$ and γ-Al_2O_3 is very weak (flat isotherm), which suggests physisorption, $Pt(acac)_2$ in fact chemisorbs with the concomitant formation of $[Al(acac)_x]_s$ [1], a conclusion corroborated by the DSC results (Fig. 1, curves b and c) in which the T_{max} of the exotherm, 290–300 °C, lies between those observed for Pd and Fe. In the $Ru(acac)_3/Al_2O_3$ system, on the other hand, only physisorption occurs although the DSC curve is very unlike its SiO_2 counterpart (compare Fig. 3, curve 3 and Fig. 2, curves e and f). The first exotherm is not associated with any significant weight loss, and indeed MS detected no desorbing species. We hypothesize that the chemisorption reaction with the c.u.s. Al^{3+} sites occurs at around 200 °C. With most other acac complexes, this reaction takes place during the adsorption experiment (see above). This implies that the reaction

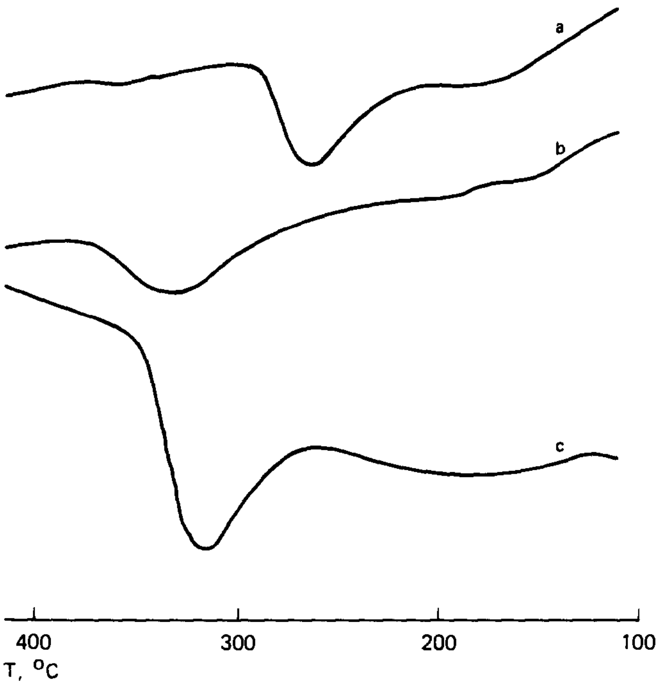

Fig. 5. DSC signals of TiO_2-supported complexes: a, $Ru(acac)_3$; b, $Pd(acac)_2$; c, $Fe(acac)_3$.

of $Ru(acac)_3$ with those c.u.s. Al^{3+} sites is easier than with the surface hydroxyls (the latter reaction occurs only in the SiO_2 case at 290 ° C, discussed above). A weight loss, corresponding to the total amount of acac present in the sample, is associated with the second exotherm at 270 ° C (product, acetone).

TiO_2

Both $Ru(acac)_3$ and $Pd(acac)_2$ simply physisorb on TiO_2, and show similar DSC (Fig. 5) and TG curves. Acetone was the only product detected by MS. This poses a problem in that the observed weight loss indicates that virtually all acac is removed in the exothermic process, in agreement with the IR results which showed that no carbonate or carboxylate species remained after the DSC/TG run ($T_{max} \approx 600 ° C$). Maybe the missing mass leaves the catalyst as O_2 and/or CO *. It is noteworthy in this respect that Jasim and Hamid [3] observed the evolution of O_2 upon heating samples of $VO(acac)_2$, $Co(acac)_2$ and $Ni(acac)_2$ in an inert atmosphere. They also observed the formation of amorphous carbon, however, which occurs rarely, if at all, in the supported systems. This is no doubt due to the fact that the

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* Unfortunately, $m/z = 28$ was not normally recorded because of the air background.

oxide surface can in principle supply the H atoms necessary for the "clean" decomposition of acac, e.g.

$$Pd(C_5H_7O_2)_2 + 2(H_2O)_s \rightarrow Pd + 3C_3H_6O + CO + O_2 \qquad (6)$$

Nevertheless, where a simple H-transfer to form acacH was observed in the SiO_2 case, eqn. (1), the reaction on a TiO_2 surface appears to be considerably more complicated (unless, of course, acacH is in fact the primary product, and is subsequently completely converted; however, the interaction of acacH with TiO_2 is not nearly as strong as that with, e.g., γ-Al_2O_3).

Strong chemisorption on TiO_2 is observed in the case of $Fe(acac)_3$ which reacts with all surface OH groups present with the formation of an $Fe(acac)_x$ surface species [8]. In the DSC curve, Fig. 5, curve c, two exotherms are seen, one broad and shallow at ~ 200 °C, and another at ~ 320 °C, most of the weight loss being associated with the latter process. In both cases, MS detected acetone only. As there are no hydroxyls left for "clean" decomposition, one would expect the formation of a carbonaceous residue, and indeed the ex-MS sample is grey. In contrast, the SiO_2-bound Fe(acac) in producing acetone hardly leaves any residue on the surface (see above) and, thus, behaves in a similar manner to the TiO_2-physisorbed $Pd(acac)_2$ and $Ru(acac)_3$ complexes just discussed.

$Ni(acac)_2 \cdot 2H_2O$

Adsorption of $Ni(acac)_2 \cdot 2H_2O$ was effected from THF solution and this turned out to be problematic in that such solutions develop a precipitate at longer times (a few weeks or so). The IR spectrum of the precipitate is dominated by a large broad band at 1590 cm^{-1}, and this feature is present in the spectra of $Ni(acac)_2$/support samples as well. On γ-Al_2O_3 the (surface) precipitate * behaves as an adsorbed species as far as its thermal behaviour is concerned: the DSC signal resembles that of $Fe(acac)_3$, compare Fig. 3, curve f, and the desorption product was simply acetone. On SiO_2, however, it appears that the surface precipitate is subject to ageing: taking an adsorption time of 4 h or one month does not make too much of a difference to the DSC curve (Fig. 2, g and h), but the desorption products were widely different. In the former case, the usual acetone was formed, but in the latter case, at low temperatures, dihydrofuranone (which supposedly derives from solvent molecules that have been incorporated in the surface precipitate), and mainly CO_2 at ~ 380 °C, were produced. The production of CO_2 has previously been observed for unsupported $Ni(acac)_2$ [3]. It is

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* We employ the term "surface precipitate" because loadings are not so high as to indicate the presence of multilayers, and also because this phase is present even after very short ($\frac{1}{2}$ day) adsorption times.

striking that in no case was acetaldehyde detected, although it features so strongly in the decomposition of unsupported chelates [3].

Gas atmosphere in the thermobalance

Unexpectedly, the amount of O_2 remaining in the N_2 (or Ar) plays a large role in determining the precise form of the DSC signal, as exemplified in Fig. 6. The sharp exotherm, characteristic of physisorbed Pd(acac)$_2$ on γ-Al_2O_3 and SiO_2, only emerges with 10–20 ppm O_2 in the gas phase. It is not clear why such a small quantity of oxygen, which affects the TG curves only very slightly (γ-Al_2O_3), if at all (SiO_2), should have such a pronounced influence on the peak shape of the exotherms.

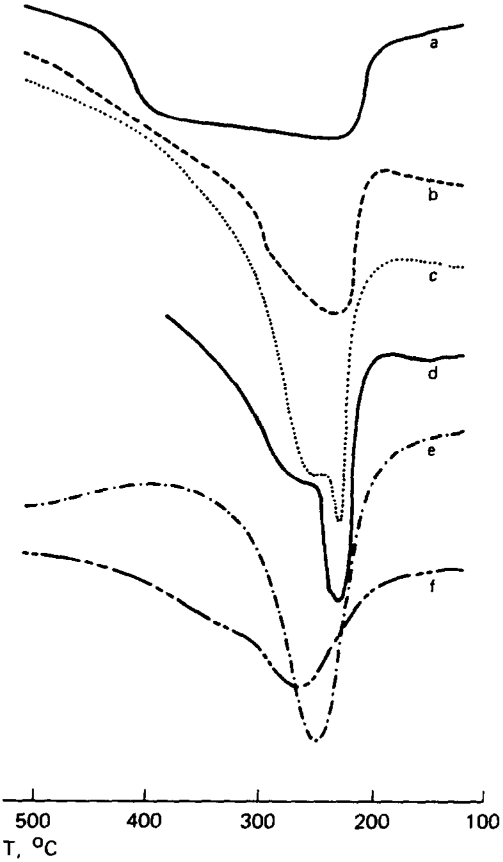

Fig. 6. Influence of gas atmosphere on the shape of the DSC signal. Pd(acac)$_2$/Al_2O_3, containing physi- and chemisorbed complex: a, Ar, O_2-free; b, N_2, 5 ppm O_2; c, N_2, 20 ppm O_2; d, N_2, O_2 content not determined; e, Ar, 10% O_2. Pd(acac)$_2$/Al_2O_3, containing only chemisorbed complex: f, as b–e above.

CONCLUSIONS

The thermal behaviour of SiO_2-, γ-Al_2O_3- and TiO_2-supported M(acac)$_n$ complexes was found to depend on three parameters: the adsorption state (i.e. whether the compound is physisorbed, chemisorbed or even precipitated), M, and the support. For SiO_2, H transfer from surface hydroxyls to the acac ligand was virtually the only reaction observed, while for TiO_2 and γ-Al_2O_3, the decomposition patterns were more complex. This should be related to the fact that the former surface consists almost exclusively of acidic OH groups, while the latter also contain basic OH groups and c.u.s. metal ions [9]. Even in the γ-Al_2O_3 case where all samples contain only an Al(acac)$_x$ surface species, M influenced (catalysed) the decomposition behaviour of that species to different extents, whatever the M(acac)$_n$ precursor.

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