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Temperature-programmed oxidative decomposition (TPOD) technique for the characterisation of supported metal clusters: a comparison with differential thermal gravimetry (DTG) technique

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Abstract

The surface chemistry of supported organometallic clusters as precursors of heterogeneous catalysts is investigated by means of DTG (differential thermal gravimetry) and TPOD (temperature-programmed oxidative decomposition) techniques, as unique signatures of the occurrence of chemical interactions between the organometallic cluster and the surface sites of the support.

INTRODUCTION

The use of organometallic clusters deposited on inorganic solid supports, as precursors of new, high-performance heterogeneous catalysts, is gaining wide acceptance in the scientific community [1–4].

However, cluster aggregation and the growth of large metal particles are often observed during the decomposition of the molecular precursor to the metal, because of the formation of highly mobile intermediate species. This undesired pathway can be avoided by anchoring chemically the molecular cluster precursor to the surface by the formation of chemical bonds [5,6]. Therefore, these chemical interactions, generally referred to as "cluster–support interactions", are likely to play a major role in determining the size and composition of the metal particles in the final material.

In this paper, we present a new and convenient thermoanalytical method for studying the occurrence of the above mentioned cluster–support interactions, by the comparative investigation of the thermal behaviour of the molecular cluster precursor using differential thermal gravimetry (DTG) and thermal programmed oxidative decomposition (TPOD) techniques. The two possible situations have been investigated:

(i) the absence of cluster–support interactions, as in the $Ir_4(CO)_{12}/SiO_2$ system [7]

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(ii) the presence of cluster–support interactions, as in the $Os_3(CO)_{12}/SiO_2$ system [5,8].

EXPERIMENTAL

$Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$ were prepared by the literature methods [9,10]. The pure carbonyl compounds were studied by differential thermal gravimetry (DTG) on a conventional, computer-controlled thermogravimetric apparatus (Du-Pont 1090 thermal analyser). The sample (2–5 mg) was heated in flowing dry air (30 ml min^{-1}) from 50 to 400 °C with a heating rate of 3 °C min^{-1}. Weight losses were calculated by integration of the DTG peaks. Supported samples were prepared by impregnating the silica support (SiO_2, Aerosil 200 from Degussa Corp., 200 m^2 g^{-1} surface area) by the incipient wetness technique with a saturated solution of the organometallic precursor in CH_2Cl_2, to give a metal loading of 2% by weight in all the final materials. Full details of the sample preparation and characterisation by FTIR have been reported elsewhere [8].

Temperature-programmed oxidative decomposition (TPOD) analyses were performed on a home-made, computer-controlled flow apparatus. The sample, as fine powder, was heated in a constant flow of $O_2(2\%)/He$ mixture (10 ml min^{-1}) from 30 to 400 °C at a heating rate of 2 °C min^{-1}.

The thermal decomposition of the supported organometallic cluster was studied by monitoring, via on-line gas chromatography, the evolution of the decomposition products, CO and CO_2, as a function of the increasing temperature. A very sensitive detection method should be employed in such studies in order to follow effectively the decomposition kinetics. The concentrations of CO and CO_2 in the effluent stream have to be kept below 0.5% for the following reasons:

(i) to minimise readsorption phenomena which would lead to peak asymmetry [11] and deviation from the theoretical gaussian shape [12].

(ii) to ensure differential conditions of CO conversion to CO_2, see, for example, ref. 13.

For this purpose, a methanation converter was placed downstream of the GC column, in order to transform CO and CO_2 into methane. The sub-ppm detection of the two components by a flame ionisation detector (FID) was thus achieved. Full details of the analytical apparatus for temperature-programmed (TPDE, TPOD) studies have been reported elsewhere [14,15].

RESULTS AND DISCUSSION

The investigation of the thermal decomposition in an oxidisng environment required the use of two different analytical techniques because of the different physical nature of the two sets of samples, the pure clusters and the supported clusters. Differential thermal gravimetry (DTG) has proved to be

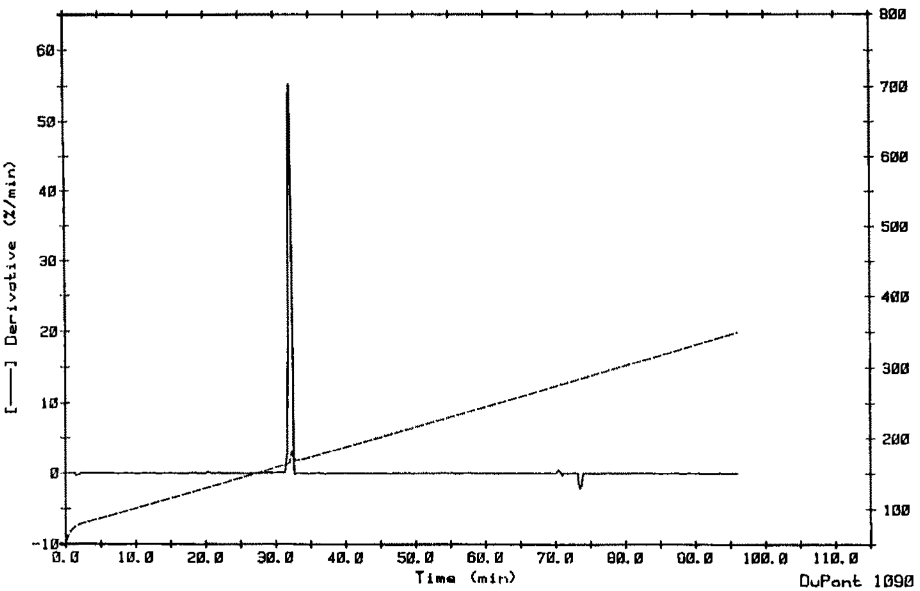

Fig. 1. DTG profile in flowing air of pure $Ir_4(CO)_{12}$.

the most convenient technique to study the pure cluster compounds (Figs. 1 and 2), as mentioned above.

In contrast, DTG gave poor results in the case of the supported samples. Large quantities of physisorbed and chemisorbed water evolved from the surface of the silica support virtually mask the weight losses due to the

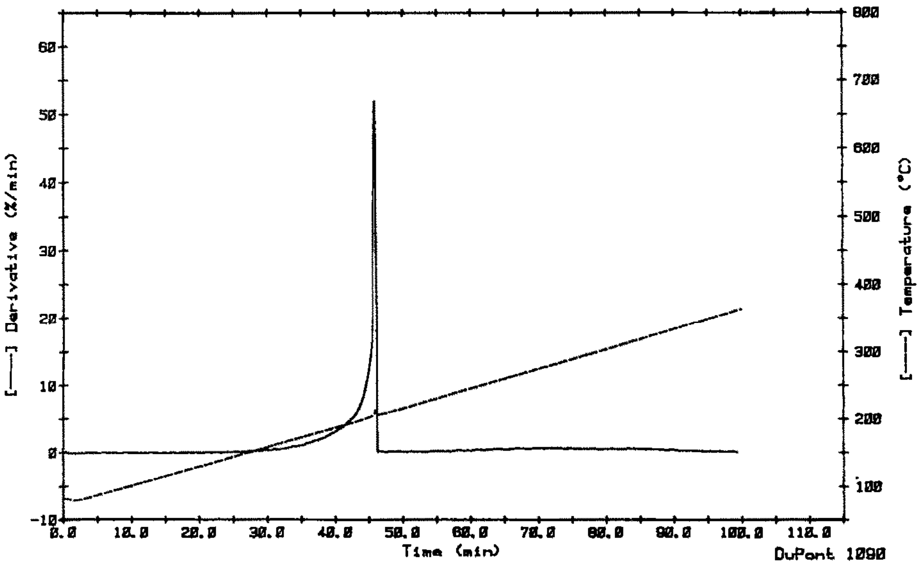

Fig. 2. DTG profile in flowing air of pure $Os_3(CO)_{12}$.

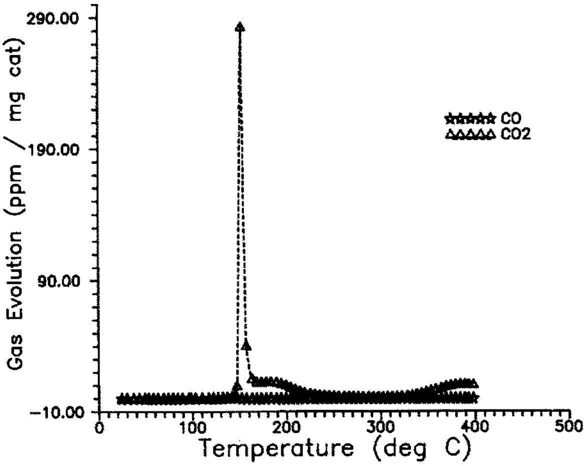

Fig. 3. TPOD profile in flowing O_2/He mixture of 2% $Ir_4(CO)_{12}$ supported on SiO_2.

decomposition of the supported carbonyl. The thermal behaviour of the supported cluster is best studied by monitoring the evolution of the gaseous decomposition products, CO and CO_2, as a function of the increasing temperature. By analogy with the already known temperature-programmed decomposition (TPDE) technique [15], this method was named temperature-programmed oxidative decomposition (TPOD) as it is conducted in an oxidising environment. In this way, an effective monitoring of the thermoanalytical behaviour of the supported material was obtained because of the highly-sensitive detection of CO and CO_2 by the combined FID–methanation converter design (see above).

From the reported DTG profiles (Figs. 1 and 2), it can be seen that all the investigated clusters readily decompose in air over a very narrow temperature range, 209 °C for $Os_3(CO)_{12}$ and 178 °C for $Ir_4(CO)_{12}$. In the case of the Os cluster, decarbonylation is accompanied by further oxidation to volatile OsO_4. A weight loss of 99% could be inferred by integration of the DTG peak, in accordance with the complete loss of osmium as OsO_4. In fact, no solid residue was left, either in the sample-holder or as sublimed $Os_3(CO)_{12}$ downstream, on the cold part of the TG reactor.

In contrast, $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ show a completely different behaviour in TPOD when supported on the surface of silica (see Figs. 3 and 4). For silica-supported $Ir_4(CO)_{12}$, cluster decarbonylation to metal occurred in a very intense narrow peak at 155 °C (Fig. 3). The supported Ir cluster thus shows a decomposition profile in TPOD that is remarkably similar to that of the pure cluster in DTG (compare Figs. 1 and 3). This observation indicates that the same decomposition pathway is taking place for the pure and the supported metal cluster. Consequently, the absence of any chemical interaction between the cluster precursor and the support is inferred by the similarity of the thermal behaviour of the cluster precursor before and after

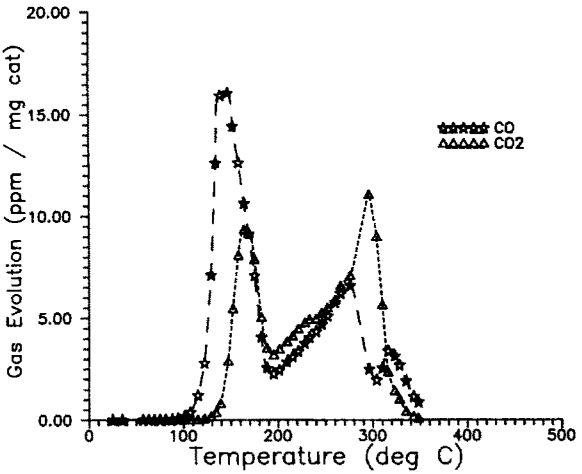

Fig. 4. TPOD profile in flowing O_2/He mixture of 2% $Os_3(CO)_{12}$ supported on SiO_2.

deposition onto the silica support. In other words, the silica support only acts as a dispersing medium for the organometallic cluster. The same conclusions have been reached by independent FTIR and XPS investigations carried out in our laboratories [7]. In further agreement with the spectroscopic results, the easier formation and stabilisation of very small (and active) Ir particles on the silica surface is likely to explain the slightly lower thermal stability of SiO_2-supported $Ir_4(CO)_{12}$ compared to that of the pure cluster. CO_2 is the only product detected in appreciable amounts during the thermal decomposition, its formation being related to activation of the O_2 molecule by the small Ir particles.

In contrast, the thermal decomposition of $Os_3(CO)_{12}/SiO_2$ in oxygen is very complex (Fig. 4). Broad peaks of CO and CO_2 evolution are observed above 100 ° C. In addition, gas evolution above 220–230 ° C is accompanied by formation of volatile OsO_4, detected by passing the gaseous effluent downstream through an aqueous KOH trap [16]. In this case, the difference with the oxidative decomposition of pure $Os_3(CO)_{12}$ in DTG is striking (compare Figs. 2 and 4). The pure cluster is in fact stable at a much higher temperature than the supported one (180–185 ° C against 100–105 ° C). Consequently, evidence of the chemical interaction of the $Os_3(CO)_{12}$ cluster with the surface sites of the silica support is readily provided by the comparison of the thermal behaviour before and after deposition onto the support. However, a better knowledge of the chemical processes occurring on the surface will require a more detailed analysis of the gas evolution in TPOD in combination with other spectroscopic techniques, such as FTIR and XPS. In fact, the first CO peak reveals a complex structure, with a maximum at 138 ° C and an evident shoulder at about 165 ° C. A spectral deconvolution was then carried out on the basis of the TPO data reported by

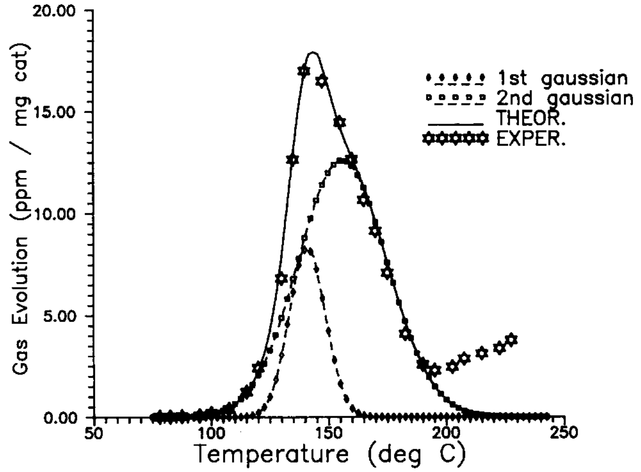

Fig. 5. Spectral deconvolution of the low-temperature peak of CO evolution of Fig. 4.

Augustine et al. under similar experimental conditions [12]. The result is shown in Fig. 5. The experimental peak of CO evolution could be resolved into two gaussian peaks, with maxima at 142 and 158 °C, respectively. It is noteworthy that the low-temperature component of CO evolution at 142 °C cannot be due to reaction with oxygen: in DTG (Fig. 2), $Os_3(CO)_{12}$ is shown to be stable in O_2 atmosphere up to about 180 °C. In addition, the absence of CO_2 formation in this temperature range rules out any reaction mechanism involving O_2 chemisorption. Previous XPS and FTIR investigations have, in fact, shown that $Os_3(CO)_{12}$ readily reacts with the –OH groups of the silica surface between 100 and 140 °C, leading to the formation of the newly grafted hydrido-cluster $HOs_3(CO)_{10}(OSi\leqslant)$, which is bonded covalently to the surface by Os–O–Si bonds [5,8].

This surface reaction is the necessary intermediate step which initiates the oxidation process of the Os_3 framework, leading to the mononuclear $[Os^{II}(CO)_x(OSi\leqslant)_2]_n$ ($x = 2,3$) surface species [8,15], and finally to OsO_4 above 220 °C [17]. The formation of surface-anchored molecular intermediates via chemical interaction with the surface can modify completely the pattern of cluster decarbonylation under oxidizing conditions. Consequently, comparison of the thermal behaviour before and after deposition onto the support predicts the occurrence of chemical interactions between the organometallic precursor and the surface of the support.

It should be possible to obtain similar conclusions working in an inert atmosphere. However, cluster decomposition in an inert stream is not a straightforward process. Formation of a high nuclearity species by aggregation of partially decarbonylated fragments during thermal decomposition to the metal is a common process in cluster chemistry, leading to very broad and complex patterns in DTG [18]. In the case of $Os_3(CO)_{12}$, such high nuclearity species, $Os_6(CO)_{18}$ in particular, tend to sublime in the TG conditions, being recovered on the cold part of the TG reactor. Therefore, in the case of supported clusters, such nucleation processes are likely to mask, at least partially, the parallel reactions of chemical interaction with the support. For SiO_2-supported osmium clusters, the competition between the two pathways has been studied and found to be strongly dependent on the experimental conditions. In particular, high loadings of the metal precursor in the supported material and very high heating rates tend to favour nucleation processes that are faster and occur at higher temperatures than interaction with the support [19]. Consequently, the investigation of the thermal decomposition of carbonyl clusters must be conducted in oxidising environments in order to suppress aggregation processes to higher nuclearity species, and to encourage cluster–support interactions.

CONCLUSIONS

A new thermoanalytical technique, named TPOD (Temperature-Programmed Oxidative Decomposition), has been developed and applied to the study of the thermal decomposition of supported carbonyl clusters.

The comparative investigation of the thermal behaviour of the organometallic carbonyl cluster before and after deposition onto the inorganic support is shown to be a unique signature of the occurence of cluster–support interactions.

The use of an oxidising environment is a necessary requirement, in order to minimise reactions of cluster aggregation to high nuclearity compounds. These reactions, which only occur under inert environments, would tend to mask the simultaneous processes of chemical interaction with the active sites of the support.

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