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Thermochemical mass-spectrometric investigation under reducing conditions of [Pd(acac)$_2$] adsorbed on magnesium oxide

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Abstract

The thermochemical behavior of [Pd(acac)$_2$] adsorbed onto different magnesium oxides has been studied under reducing conditions by means of the TPRD (temperature-programmed reductive decomposition) technique coupled to mass spectrometry. The thermal profiles of the different decomposition products have been rationalized in terms of chemical interactions with the support, and correlated with the catalytic properties in the dehydrocyclization reaction of *n*-heptane.

The technique is then proposed to be a valid screening methodology for routine testing of catalytic batches without the need of running costly and time-consuming catalytic tests. © 1998 Elsevier Science B.V.

Keywords: TPRD; Thermoanalytical studies; Palladium catalysts; Mass spectrometry; Surface decomposition

1. Introduction

The recent advances in solid-state electronics [1] and catalysis [2] have been often achieved through the utilization of organometallic complexes as precursors of high-purity metal phases with the desired composition and topology. In this respect, acetylacetonate complexes have a significant role [3–5], since they are easily synthesized and/or purified, and their volatility may be finely tuned for CVD applications by the controlled introduction of fluorine atoms. Moreover, the supported metal phase is simply obtained by controlled thermal removal of acetylacetonate ligands. However, the final properties of the metal phase, particularly for catalytic purposes, are generally dependent on the nature of the chemical interactions between the organometallic complex and the oxide support [3–6].

Thermochemical methods play a primary role in the characterization of the kinetics of decomposition processes of the supported organometallics to yield the desired metal phase. Many different approaches have thus been proposed, ranging from conventional DTG studies [4,5] to more specialized flow techniques for catalyst characterization [7–10]. In particular, flow techniques under reducing conditions, primarily the TPRD technique [8,9], are thought to offer significant advantages, in that they mimic the actual activation and catalytic condition of working catalysts. However, no defined correlations between such thermochemical studies and catalytic activity have been presented so

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far, preventing a wide-scale utilization of thermochemical techniques for screening purposes. There is, in fact, an increasing need of simple analytical techniques for routine prescreening of catalytic batches as an alternative to the costly and time-consuming catalytic tests.

In this paper, we will present the application of the TPRD (temperature-programmed reductive decomposition, [8,9]) technique to a series of Pd/MgO catalysts obtained from [Pd(acac)$_2$] precursors with different acid/base and metal/support properties, and, consequently, different catalytic behaviour. The information obtained from the thermal profiles will be interpreted as a function of metal/support interactions, with the final purpose of fingerprinting (and possibly predicting) their catalytic properties.

2. Experimental

[Pd(acac)$_2$] was prepared from K_2PdCl_4 as reported in the literature [11].

Reagent-grade MgO (Carlo Erba RPE) was refluxed in doubly distilled water for 2 h and dried in air at 100°C. This type of support is referred to as MgO^{air}. Highly dehydroxylated magnesium oxide (MgO^{500}) was obtained by heating MgO^{air} in air from 25 to 500°C and further evacuation (P=10^{-5} mbar) at this temperature overnight. MgO^{HCl} was prepared from MgO^{500} by treating with excess 0.9 M HCl and further drying overnight at 500°C in vacuo (P=10^{-5} mbar).

Reagent-grade $La_2O_3^{500}$ (Strem Chemicals, 99.99% purity) was treated as MgO^{500}.

Reagent-grade benzene and dichloromethane (Fluka) were dried over 5 Å molecular sieves.

The oxide supports were impregnated at room temperature under nitrogen atmosphere with a dilute solution of [Pd(acac)$_2$]. Typically, 2.0 g of MgO were impregnated with ca. 115 mg of [Pd(acac)$_2$] dissolved in 20–30 cm^3 of the solvent, in order to have a final Pd loading of 2 wt%. Benzene was generally used as solvent, although it may be safely substituted by toluene without any difference. Instead, for MgO^{500}, impregnation was conducted either in benzene and in dichloromethane.

For MgO^{500}, the solution became colourless after few hours of stirring; the yellow-coloured impregnated material was then filtered off, and dried overnight in vacuo (10^{-2} mbar). For all other supports, the solution remained lightly yellow-coloured after 24 h of stirring. The solvent was then removed in vacuo, and the sample dried overnight in vacuo.

TPRD experiment [8,9] was carried out in a flowing mixture H_2(8%)/He in a flow-through glass reactor. Conventional sample holder for thermogravimetric analyses could not be used, because of diffusion limitations of the sample bed. The temperature was raised from 25° to 500°C at 3°C/min using a computer-controlled temperature programmer (Ascon YM).

Volatile products were monitored by an on-line quadrupole mass spectrometer (VG Masstorr, 0–130 amu) interfaced by a differentially pumped capillary inlet.

Data acquisition was carried out in selected ion-monitoring mode, and presented as a function of the increasing temperature. A detailed description of the instrumental setup was reported elsewhere [9].

Catalytic tests were made on samples after the thermochemical investigation, using a continuous-flow glass microreactor. Quantitative analyses of reactants and products were carried out on an on-line gas chromatograph (Carlo Erba Instruments HRGC 5160) fitted with a thermostatted sampling valve and FID, using a 50 m, silica-fused capillary PONA column. The test reaction chosen was the catalytic dehydrocyclization of n-heptane at 500°C and 1 atm, with a H_2/C_7H_{16} ratio of 20.

3. Results and discussion

The thermal reduction profiles in an hydrogen atmosphere of pure [Pd(acac)$_2$] were monitored at m/z=15, 43 and 85 (Fig. 1). A single sharp peak for all m/z values was observed at 75°C. The signal at m/z=85, due to the $[COCH_2COCH]^+$ ion, was a typical fragmentation ion in the electron impact (EI) mass spectrum of acetylacetone; it was, therefore, indicative of the evolution of acetylacetone (acacH) following a classical reductive elimination mechanism:

$$[\mathrm{Pd(acac)_2}] + \mathrm{H_2} \rightarrow \mathrm{Pd^0} + 2\,\mathrm{acacH}$$

The signals at m/z=15 and 43, due to CH_3^+ and CH_3CO^+ ions, respectively, were instead much less diagnostic. They are related not only to the formation of acetylacetone, but also to all the possible hydro-

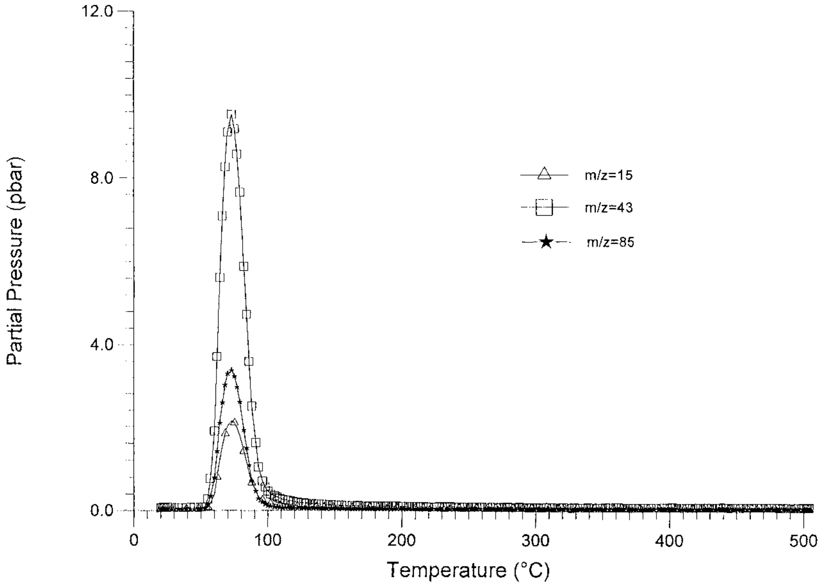


Fig. 1. TPRD profiles of pure [Pd(acac)$_2$] in flowing H_2 (8%)/He mixture.

genation products: typically, 2,4-pentadiol, acetone, propanol, and saturated hydrocarbons. However, the close similarity of the MS traces, and the absence of any other peaks at higher temperatures, suggest that only acetylacetone is evolved during the reductive decomposition of [Pd(acac)$_2$]. Moreover, the intensity ratios of the three m/z values are those expected on the basis of the electron-impact mass spectrum of acetylacetone.

Upon deposition onto a highly dehydroxylated magnesium oxide surface (MgO^{500}), the resultant material showed a totally different thermal behaviour (Fig. 2). In particular, no evolution at m/z=85 was observed, rejecting any formation of acetylacetone following the previously depicted mechanism. Instead, a broad and complex evolution of m/z=43 and 58, with two peaks at 105° and 290°C was observed. The signal at m/z=58 is attributed to the $[CH_3COCH_3]^{+}\cdot$ion radical as the parent ion in the electron impact mass spectrum of acetone. The evolution of such product was already reported in the thermal decomposition of [Pd(acac)$_2$]/Al_2O_3, albeit under slightly oxidizing conditions [5]. A gas-chromatographic analysis of the evolution products under these temperature ranges confirmed the formation of acetone, along with some isopropanol. This latter product was formed by the further hydrogenation of acetone deriving from acetylacetone adsorbed onto the palladium phase.

This evolution of acetone and isopropanol, through the surface-mediated fragmentation of acetylacetonate ligands, has the additional consequence that some organic residues are left on the surface. We suggest that this deposition takes place by two different mechanisms:

1. on the metal surface, via the polymerization of C_2 fragments, or, more generally, of C_x fragments as it is often observed in heterogeneous catalysis [12];
2. on the MgO support through the formation of acetate ions [5] at the metal oxide interface.

The evolution profile of $[CH_3]^+$ ion at m/z=15 parallels those at m/z=43 and 58 up to ca. 320°C, since the $[CH_3]^+$ fragment is present in the electron-impact spectra of acetone and isopropanol. At higher temperatures, however, an additional evolution peak at m/z=15 is observed, although no signals at m/z=43 and 58 can be seen. This observation indicates that, in this temperature range, the signal at m/z=15 can be due only to the evolution of methane. It is suggested that this formation of methane derives from the hydro-

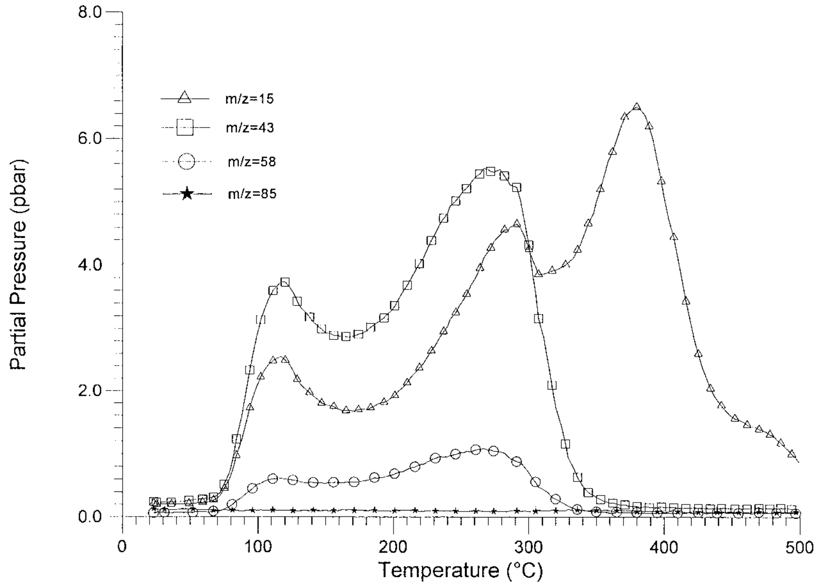


Fig. 2. TPRD profiles of $[Pd(acac)_2]/MgO^{500}$ impregnated from benzene.

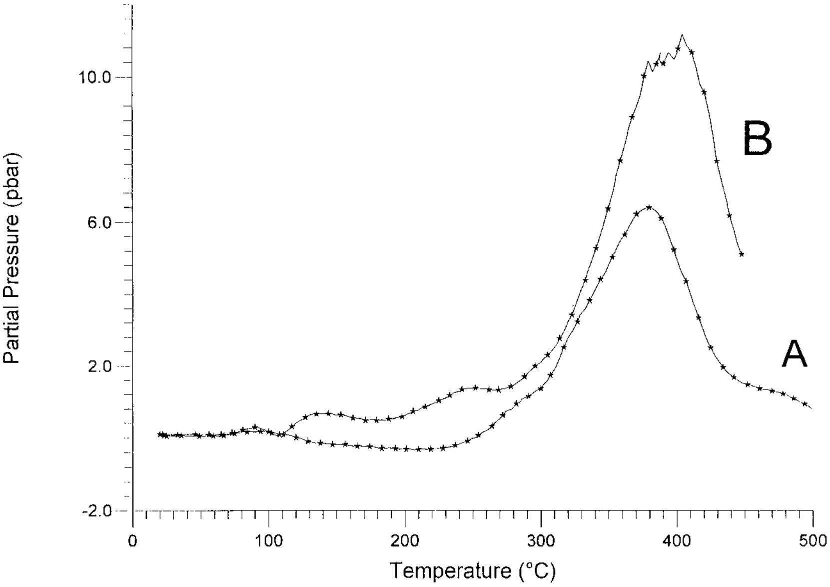
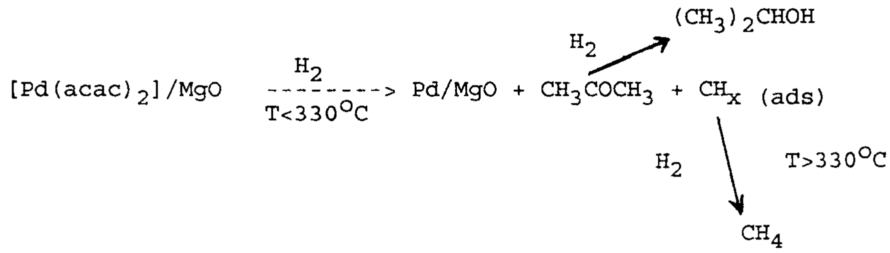


Fig. 3. Evolution profiles of methane in the TPRD of $[Pd(acac)_2]/MgO^{500}$: (A) sample prepared from C_6H_6; and (B) sample prepared from CH_2Cl_2.

genolysis of the organic residues left on the catalyst, as it is often observed in TPRD profiles of reforming-type catalysts [13].

According to this hypothesis, we subtracted the MS trace at *m*/*z*=43 from that at *m*/*z*=15, resulting in a single, broad peak of methane evolution centered ca. 400°C (Fig. 3(a)).

The overall reactivity of MgO-supported $[Pd(acac)_2]$ under TPRD conditions may be summarized as follows:



$$[Pd(acac)_2]/MgO \xrightarrow[T<330^{o}C]{H_2} Pd/MgO + CH_3COCH_3 + CH_x\ (ads)$$

$$CH_3COCH_3 \xrightarrow{H_2} (CH_3)_2CHOH \qquad CH_x\ (ads) \xrightarrow[T>330^{o}C]{H_2} CH_4$$

where $CH_{x(ads)}$ indicates the organic residues left on the surface.

This profound difference between the thermochemical behaviour of pure (unsupported) and MgO-supported $[Pd(acac)_2]$ resides in the chemical interaction between the organometallic molecule and the basic sites of the magnesium oxide surface.

In particular, the formation of hydrogenated products along with acetone, and of methane at high temperatures, may only be rationalized if we assume that the acetylacetonate ligands remain chemisorbed on the active palladium atoms. As already pointed out, the hydrogenolytic rupture of the C–C bond in the 2–3 position then leads to the evolution of acetone and isopropanol with deposition of organic residues on the catalyst, possibly at the interface between the growing palladium particles and the MgO surface, that are eventually removed as methane. We found that this type of interaction is extremely sensitive to the experimental condition and particularly to the nature of the organic solvent used for the deposition of $[Pd(acac)_2]$. In fact, a $[Pd(acac)_2]/MgO$ sample prepared from a chlorinated solvent such as CH_2Cl_2 shows a different TPRD profile at $m/z=58$, with three peaks at 105°, 218° and 295°C instead of the two-peak feature previously reported for the material impregnated from benzene (compare Figs. 2 and 4). Secondly, evolution of methane is significantly increased, starting at temperatures well below 300°C (Fig. 3(b)). We speculate that the use of a chlorinated solvent modifies the surface of MgO support. Potentiometric and infrared studies show that new, acidic Mg–Cl sites are present upon thermal activation in hydrogen [14]. These new surface sites, of Lewis acid character, offer new sites

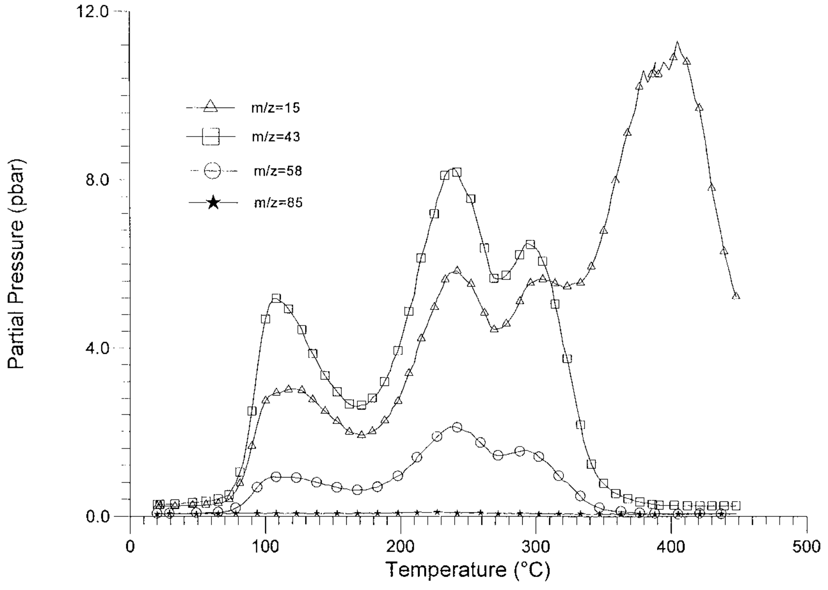


Fig. 4. TPRD profiles of $[Pd(acac)_2]/MgO^{500}$ impregnated from dichloromethane.

Table 1
The catalytic activity to *n*-heptane dehydrocyclization[a] of some supported palladium catalysts

Support	Impregnation solvent	Activity[b] (mol%)	Aromatics (mol%)
MgO^{500}	C_6H_6	70	84
MgO^{500}	CH_2Cl_2	45	83
MgO^{air}	C_6H_6	11	72
MgO^{HCl}	C_6H_6	9	58
$La_2O_3^{500}$	C_6H_6	<1	—

[a] Experimental conditions: T=500°C, P=1 atm, H_2/C_7H_{16}=20.
[b] Activity expressed as mole percent conversion of *n*-heptane to aromatics.

for the adsorption of the $[Pd(acac)_2]$ molecule, and, at the same time, cause an increased deposition of carbonaceous residues, as evidenced by the higher amount of evolved methane. The presence of surface acidity on metal catalysts is known to cause an increased carbon deposition on the surface [15].

The observed differences in the thermal reduction profiles of the two $[Pd(acac)_2]$/MgO samples are not merely instrumental effects, but are strongly related to chemical activity. The two samples at the end of the reduction treatment are in fact good catalysts for hydrocarbon reactions, particularly for the high-temperature dehydrocyclization (aromatization) reaction of *n*-heptane (Table 1). Benzene as the impregnation solvent was significantly superior to dichloromethane, leading to higher activity materials. The catalytic activity, expressed as mole percent conversion of *n*-heptane to aromatics at fixed contact time, decreased from 70 to 45% when dichloromethane was used for the impregnation of MgO^{500} support.

In addition, the data in Table 1 clearly show that the presence of a highly basic surface is the primary requirement for developing a catalytically active metal phase. The removal of highly active basic sites of MgO by exposure to air (MgO^{air}) or to hydrochloric acid (MgO^{HCl}) leads to a dramatic decrease in catalytic activity. The two palladium samples supported on MgO^{air} and MgO^{HCl} showed conversions of *n*-heptane ca. 10% only.

The thermal reduction profiles of $[Pd(acac)_2]$ deposited on MgO^{air} (Fig. 5) and on MgO^{HCl} (Fig. 6) have also been studied.

In the MgO^{air} sample, the TPRD experiment had to be stopped at 350°C, when large amounts of water and CO_2 started to be evolved from the decomposition of magnesium hydroxide and carbonate species, preventing the MS detector to work under proper conditions.

In both cases, the evolution profiles in flowing H_2/He mixture looked quite different from those of

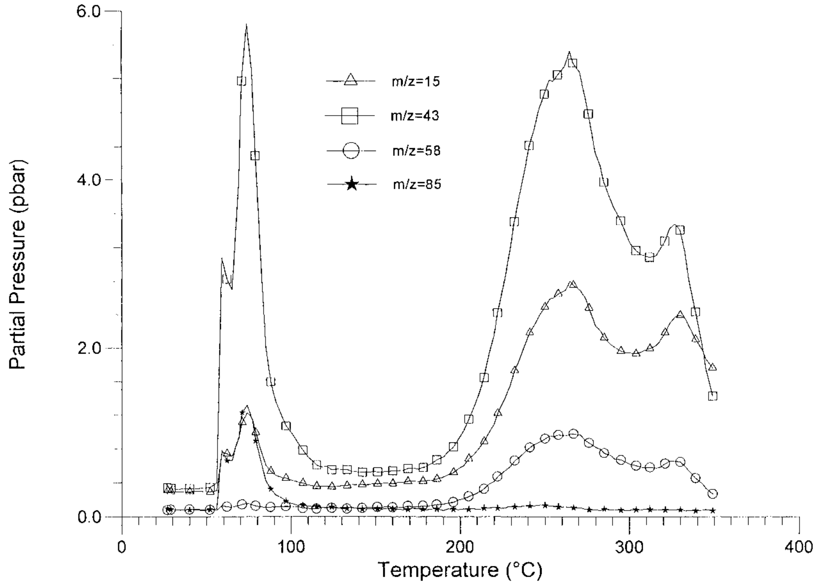


Fig. 5. TPRD profiles of $[Pd(acac)_2]/MgO^{air}$.

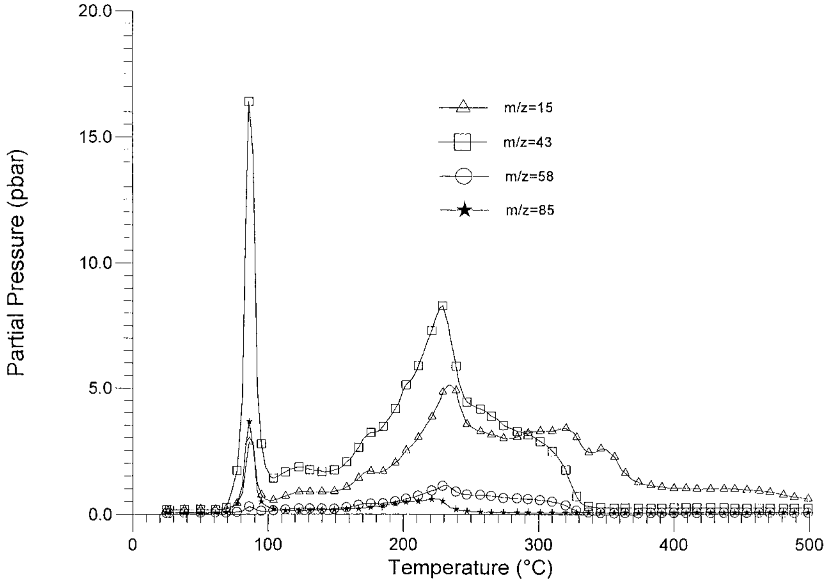


Fig. 6. TPRD profiles of [Pd(acac)$_2$]/MgO^{HCl}.

[Pd(acac)$_2$] deposited on MgO^{500}. In particular, a low-temperature peak at *m*/*z*=85 is observed between 65° and 90°C in both thermal profiles, which is due to the evolution of free acetylacetone (Figs. 5 and 6). This closely resembles the behaviour of pure unsupported [Pd(acac)$_2$] (Fig. 1). At higher temperatures, some evolution of acetone at *m*/*z*=58 was then observed below 330°C, whereas some residual methane was still formed at 500°C.

These two features, namely the evolution of acetylacetone at low temperature and the negligible methane formation from $CH_{x(ads)}$, are necessarily related to a completely different surface chemistry of [Pd(acac)$_2$]. The occurrence of a simple physisorption of the palladium precursor without any significant chemical interaction with the MgO surface is then suggested. This fact confirmed the ability of the TPRD thermoanalytical technique to differentiate between chemisorbed and physisorbed state of supported metal complexes, owing to the advantage of investigating the sample under reducing conditions, which mimic the actual working conditions of the catalyst. This surface reactivity can be explained with the dramatic decrease in surface basicity caused by surface carbonates or chlorides. The organopalladium molecule is, thus, no longer able to chemically react with the surface; as a consequence, the Pd precursor is not homogeneously distributed over the surface, and the formation of a highly dispersed, highly active metal phase is prevented. We confirmed this assumption by investigating the thermal behaviour of a Pd/La$_2$O$_3^{500}$ (Fig. 7) catalyst of very low catalytic activity. Accordingly, the evolution of acetylacetone is a key feature of the thermal profile, and demonstrates how the La$_2$O$_3$ surface is totally inert towards the adsorption of the acetylacetonate complex.

4. Conclusions

Thermochemical mass-spectrometric characterization under reducing conditions of [Pd(acac)$_2$]/MgO offers a simple analytical methodology for fingerprinting the surface properties of supported palladium phases. A complex thermal behaviour was demonstrated to be related to a strong interaction between the metal complex and the surface, and eventually to a high catalytic activity.

A simple physisorption, associated with a low catalytic activity, was instead revealed by few sharp peaks of ligand evolution.

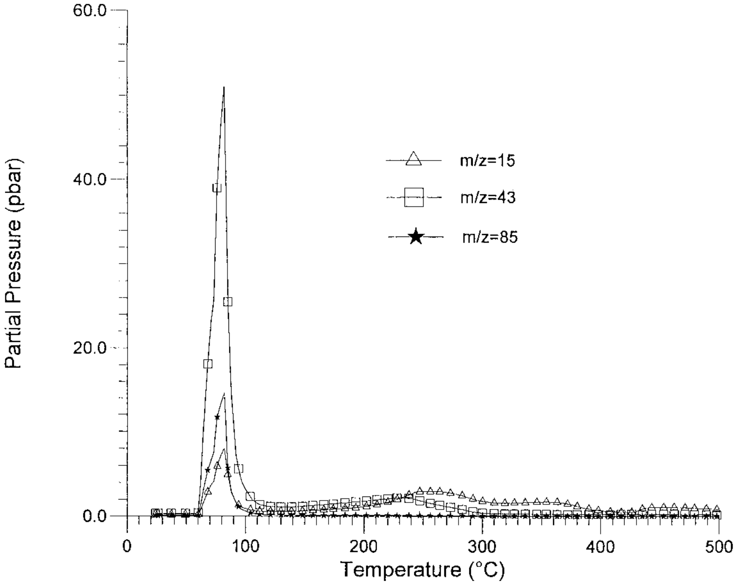


Fig. 7. TPRD profiles of $[Pd(acac)_2]/La_2O_3^{500}$.

This analytical approach could, thus, be proposed as a valid routine screening methodology of catalytic batches before running costly and time-consuming catalytic tests.

Acknowledgements

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