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THERMAL STABILITY OF A POLYMER-SUPPORTED RHODIUM CATALYST FOR METHANOL CARBONYLATION

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Abstract

A novel rhodium-containing diphenylphosphinate copolymer of styrene ad divinylbenzene (used as catalyst for methanol carbonylation) was prepared and studied by means of thermoanalytical methods. Simultaneous TG-DTA experiments were run to assess the effect of the grafting procedure on the thermal behaviour. Additional information concerning the structural modifications observed was obtained by infrared spectroscopy.

On the basis of the collected evidences the cited catalysts were found to be stable up to 250°C in the presence of nitrogen and thereafter progressive degradation took place. Such high thermal stability is consistent with the experimental conditions used (T=230°C, p_{CO+H_2}= 210 bar) for the recently reported methanol carbonylation promoted by iodomethane which leads to a mixture of C_2–C_6 carboxylic acids.

Keywords: methanol carbonylation, polymer-supported rhodium, syngas, thermal stability

Introduction

A new preparative route to short-chain aliphatic alcohols was developed where the products, optionally based upon syngas feedstocks alone, are useful as octane boosters or may be used directly as basic chemical products.

The first step involves the carbonylation of methanol to a mixture of a short-chain aliphatic carboxylic acids [1]

$$\mathrm{MeOH}+2n\mathrm{H_2}+(n+1)\mathrm{CO} \rightarrow \mathrm{Me(CH_2)_nCO_2H}+n\mathrm{H_2O}$$

in the presence of a suitable rhodium catalyst and a iodide-containing promoter. The acids are then converted through a transesterification reaction to the corresponding esters and finally to alcohols by hydrogenolysis.

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Due to the drastic experimental conditions (long term runs performed continuously at 230°C and 210 bar), the use of lanthana-, silica-, thoria-, or alumina-supported rhodium catalysts for methanol carbonylation is hampered by a slow leaching out of the rhodium complex which makes the catalysts unattractive for industrial use. Better results are obtained with chemically anchored rhodium complexes on polymeric [2–4] supports or with rhodium supported on activated carbon.

The use of polymers as support for catalytic reactions is a relatively unexplored area. With differently functionalized polymers it is possible to modify the interactions with the catalytic precursor and thus affect the morphology of the resulting catalyst. Considering the polymer as a very large 'ligand', one might also expect changes in activity and selectivity by changing these 'ligands' comparable to what is found in homogeneous catalysis.

For the cited methanol carbonylation a prerequisite of the application of a polymeric support is an appropriate thermal stability. We wish to report here on a study which was carried out in order to assess the thermal stability of a commercially available (FLUKA) diphenylphosphinated copolymer of styrene and divinylbenzene (indicated hereafter with SDT) as such or grafted with rhodium as catalyst [3].

Experimental

Grafting procedures

The fixation of two rhodium precursors $Rh_2Cl_2(CO)_4$ and $Rh_4(CO)_{12}$ on the diphenylphosphinated copolymer of styrene and divinylbenzene (SDT crosslinked with 2% DVB: ≈3 mmol triphenylphosphine/g resin; 200–400 mesh) has been recently reported [2]. With the cited organometallic compounds after the grafting reaction no appreciable modification of the copolymer was detected by analysing the soluble fractions. Slight variations of the degree of crosslinking or the number of functional groups (using, e.g., SDT crosslinked with 1% DVB; ≈1.4 mmol triphenylphosphine/g resin; 100–200 mesh) do not affect the grafting procedure. The fixation of the promoter (CH_3I) on the same catalysts has also been reported [2].

$Rh_2Cl_2(CO)_4$ was commercially available (FLUKA) and used as such while $Rh_4(CO)_{12}$ was synthesized by Professor Philippe Kalck (ENSCT-Toulouse).

TG-DTA and IR analyses

Under an inert atmosphere (nitrogen), the thermal behaviour of the unsupported (SDT) or Rh-supported SDT/$Rh_2Cl_2(CO)_4$ or SDT/$Rh_4(CO)_{12}$ polymeric resin was carefully monitored: 1) from room temperature up to over 250°C at a heating rate of 20°C min^{-1} and 2) under isothermal conditions by heating the specimen at 180°C for 20 h.

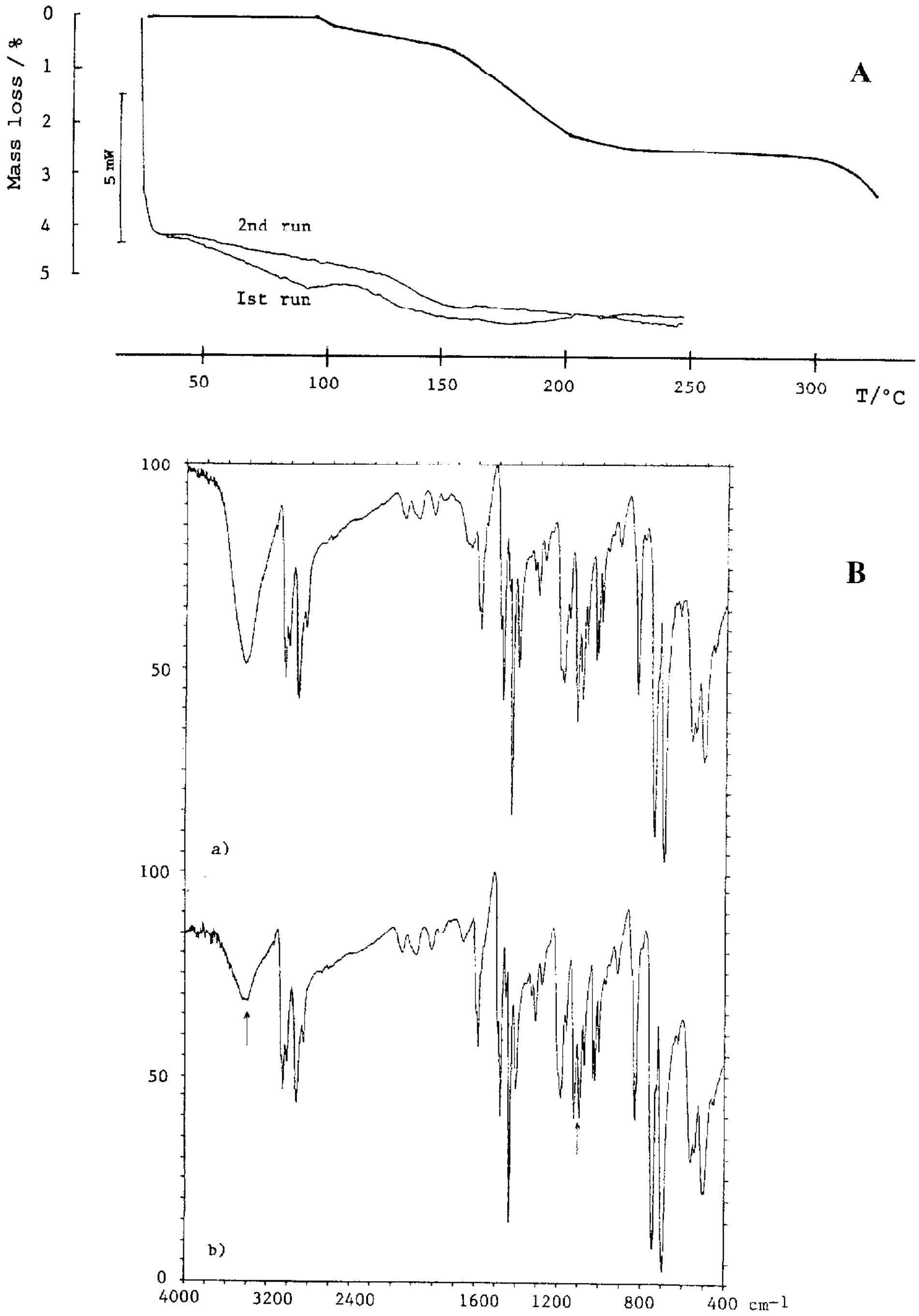

Fig. 1 A: SDT resin, TG and DTA traces under N_2 flow; B: IR spectra: (a) as such, (b) heated over 250°C under N_2

Before and after each thermal run all specimens were analyzed at room temperature by IR spectroscopy in KBr pellets.

Results and discussion

The results of the TG-DTA tests of the unsupported (SDT) polymeric resin are reported in Fig. 1A. In an inert atmosphere, up to over 250°C negligible mass losses (<3%, wt/wt) are observed which may be attributed to the elimination of small amounts of weakly bound water (Fig. 1B): the absorption at ca. 3450 cm^{-1} due to the OH stretching vibration decreases. Other typical absorptions such as the C–C aromatic stretching between 1600–1480 cm^{-1} or the C–H aromatic stretching between 3050–3000 cm^{-1} do not change. Furthermore, it may be observed (Fig. 1A, the DTA scans) that in the first run a broad peak at about 120°C can probably be attributed to an additional crosslinking reaction induced by thermal treatment. In accordance with these assumptions, in the second run this peak disappears and T_g moves to higher temperatures relative to the corresponding

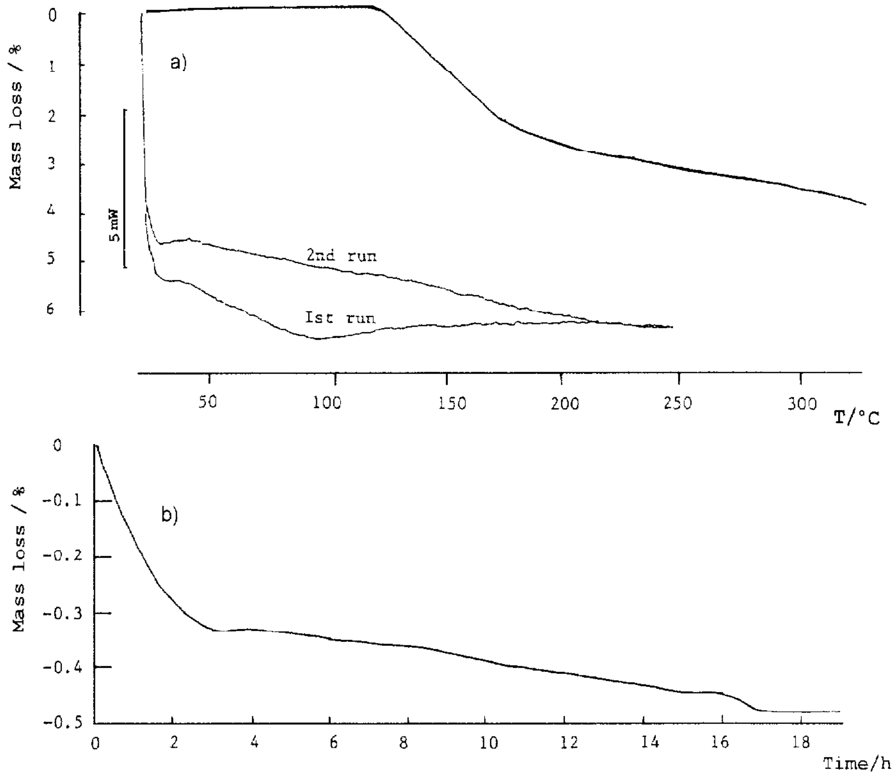

Fig. 2 [SDT/$Rh_2Cl_2(CO)_4$: 4% wt/wt] catalyst, (a) TG and DTA traces under N_2 flow; (b) under isothermal conditions at 180°C

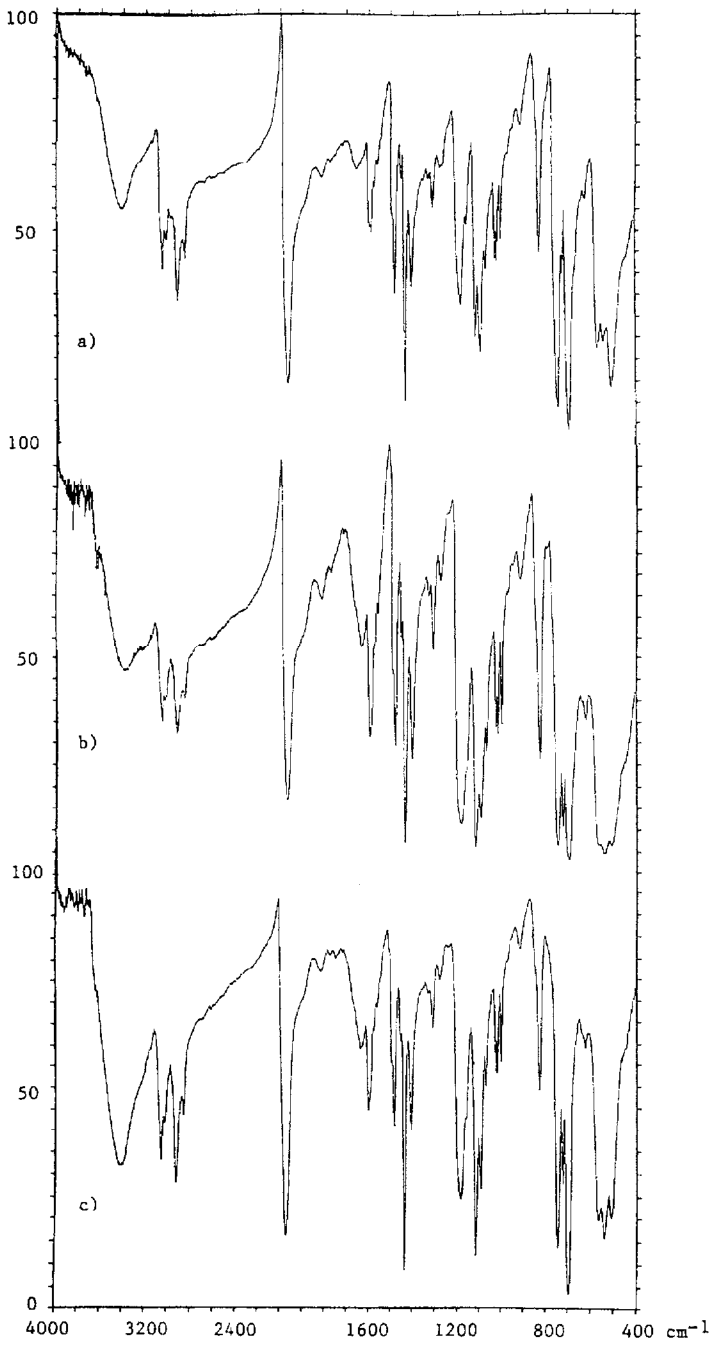

Fig. 3 [SDT/$Rh_2Cl_2(CO)_4$; 4% wt/wt] catalyst, IR spectra: (a) as such, (b) heated over 300°C under N_2, (c) after 20 h at 180°C

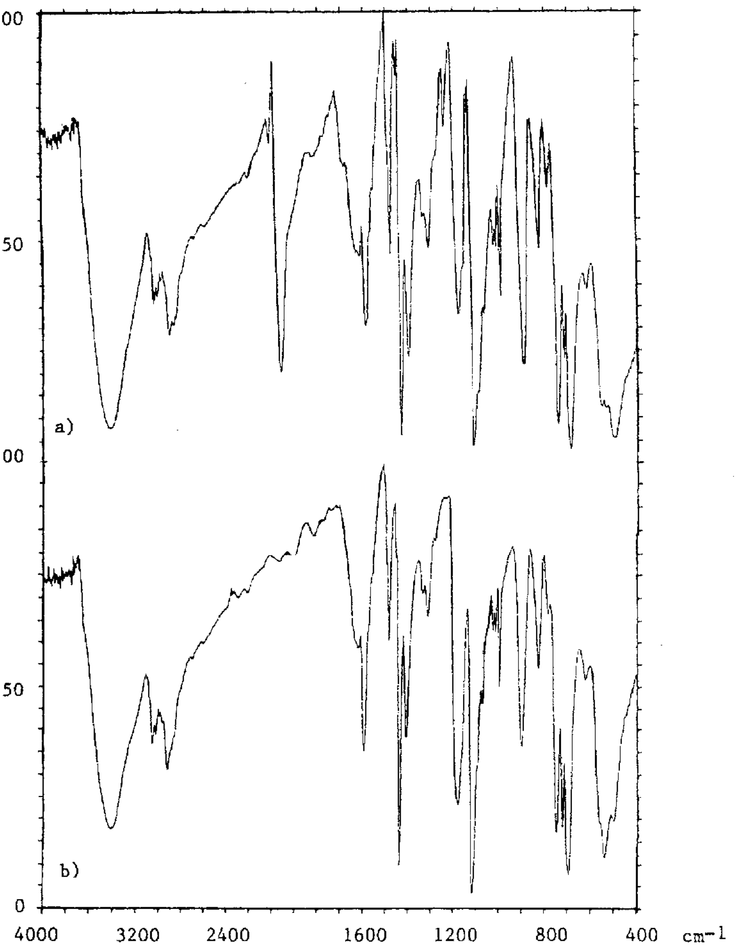

Fig. 4 Iodomethylated [SDT/$Rh_2Cl_2(CO)_4$] catalyst, IR spectra: (a) as such, (b) heated over 300°C under N_2

value observed in the first run. Similar considerations are less evident when (see, e.g., Fig. 2a and in particular Figs 5, 6a and 9) using grafted catalysts.

Referring now to the SDT/$Rh_2Cl_2(CO)_4$: 4% wt/wt even at temperatures higher than 300°C, the minor (≈3% wt/wt) mass losses observed (Fig. 2a) can hardly be attributed as before to the elimination of weakly bound water and do not imply significant losses in the intensity of the very strong band at 1980 cm^{-1} (Fig. 3a and b) assigned to a rhodium (I)–CO trans configuration [5].

A remarkable thermal stability is observed since on standing 20 h under isothermal conditions at 180°C, the mass losses are almost unnoticeable (Fig. 2b) while no shift of the band of the Rh(I)–CO complex to higher frequencies is de-

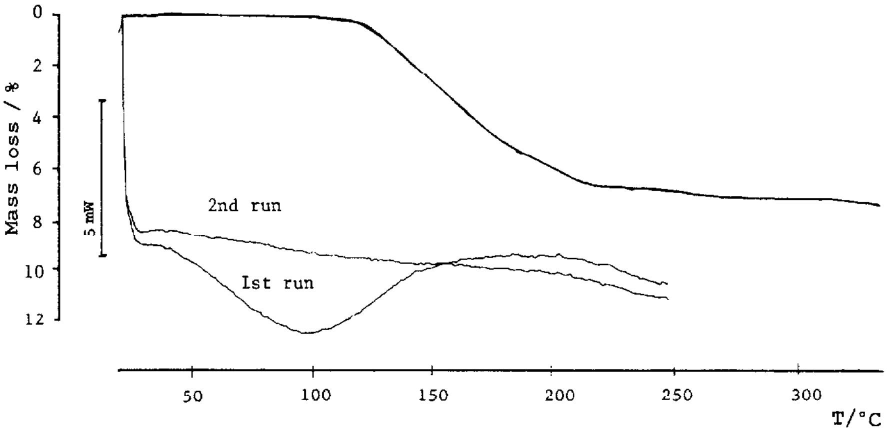

Fig. 5 Iodomethylated [SDT/$Rh_2Cl_2(CO)_4$] catalyst, TG and DTA traces under N_2 flow

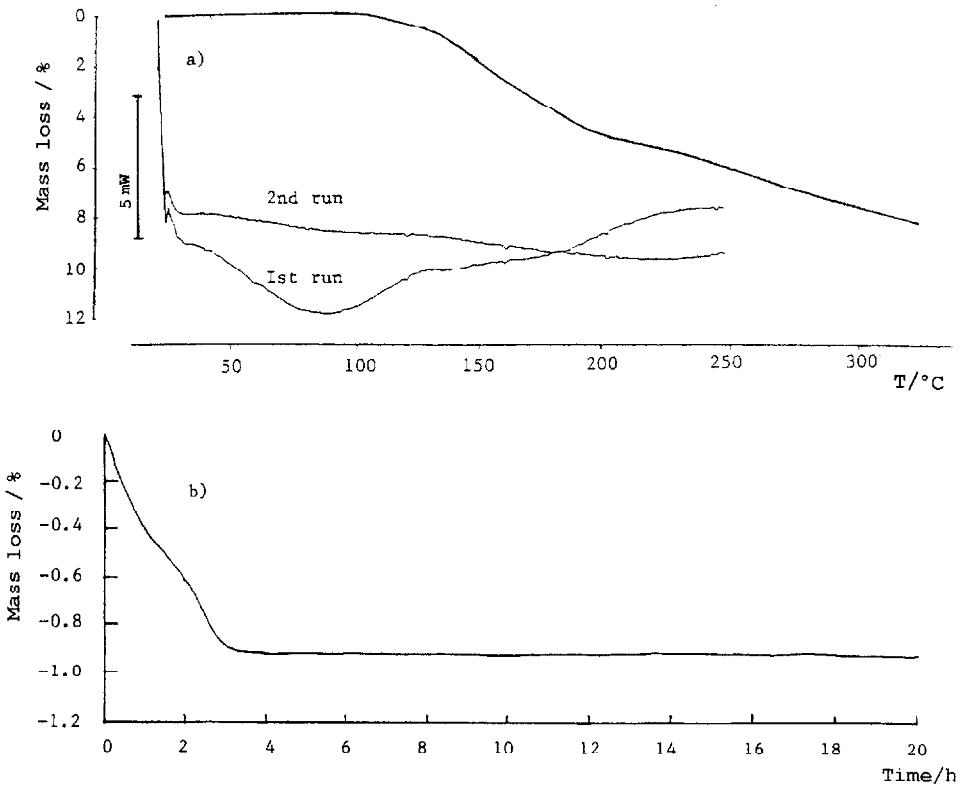

Fig. 6 [SDT/$Rh_4(CO)_{12}$: 5.1% wt/wt] catalyst, (a) TG and DTA traces under N_2 flow; (b) under isothermal conditions at 180°C

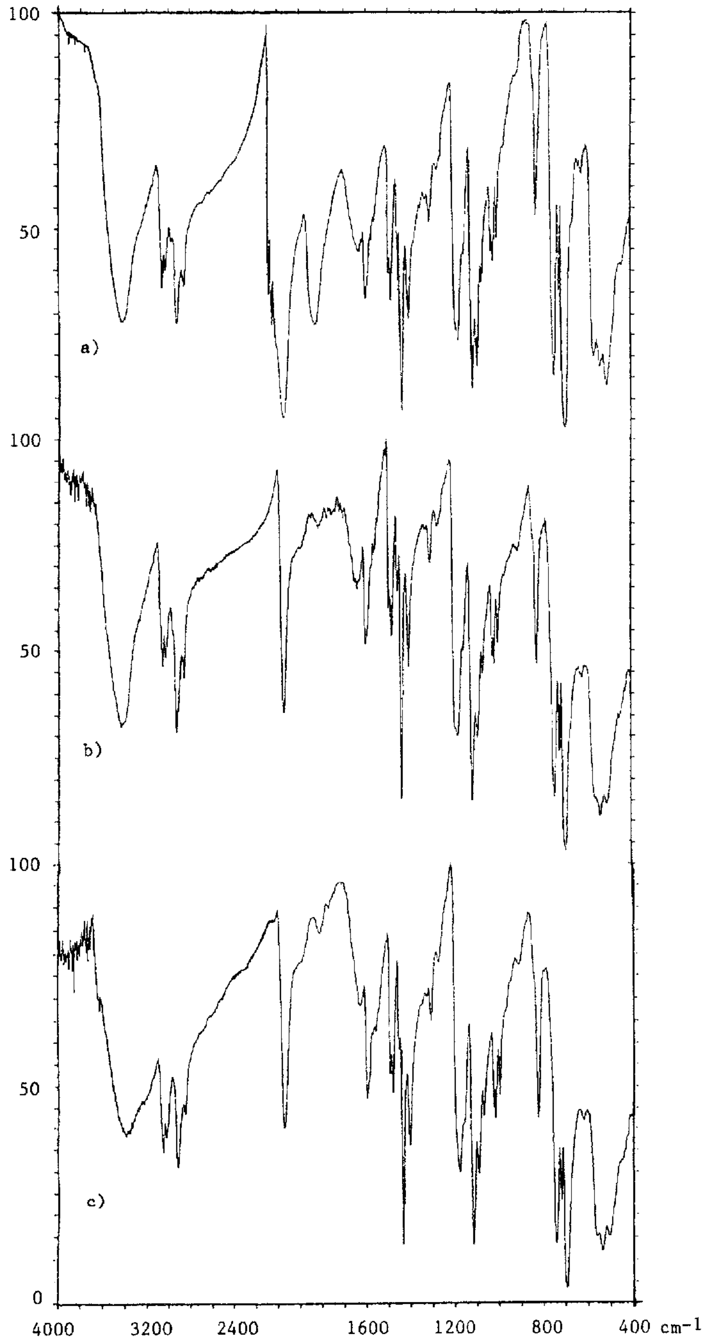

Fig. 7 [SDT/$Rh_4(CO)_{12}$: 5.1% wt/wt] catalyst, IR spectra: (a) as such, (b) heated over 300 °C under N_2, (c) after 20 h at 180°C

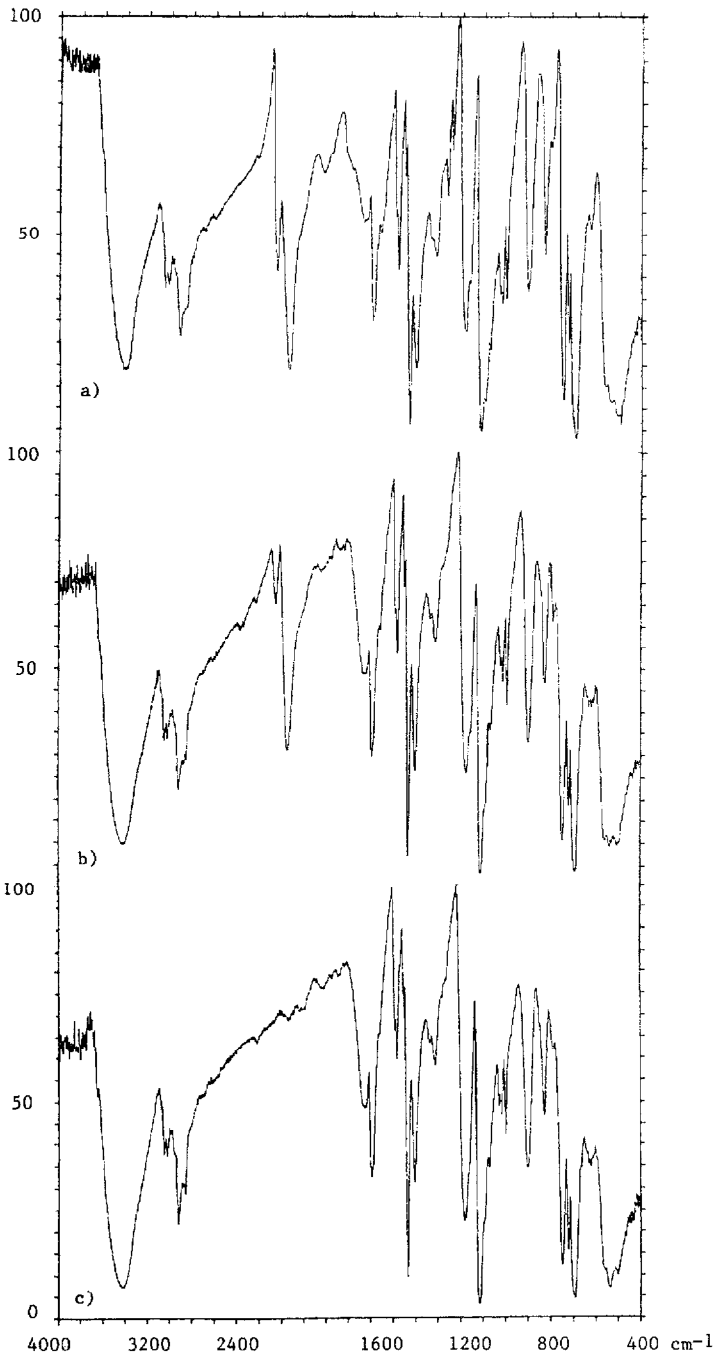

Fig. 8 Iodomethylated [SDT/$Rh_4(CO)_{12}$] catalyst, IR spectra: (a) as such, (b) heated over 200°C, (c) over 300°C under N_2

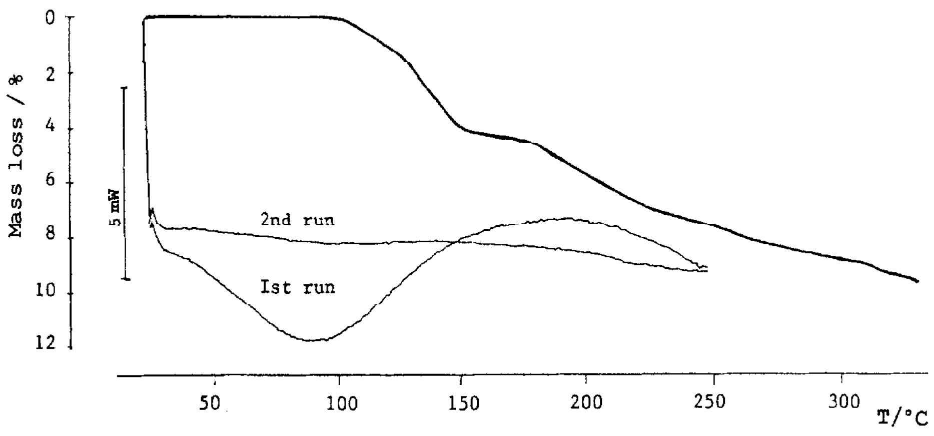

Fig. 9 Iodomethylated [SDT/$Rh_4(CO)_{12}$] catalyst, TG and DTA traces under N_2 flow

tected thus excluding any Rh(I)→Rh(III) conversion (Fig. 3c) [6]. This conversion occurs when SDT/$Rh_2Cl_2(CO)_4$ interacts with iodomethane* [7] yielding by oxidative addition a Rh(III) complex characterized by: 1) a weak band at ca. 2020 cm^{-1} (Fig. 4a) and 2) mass losses which are noticeably higher than those reported for the non-oxidized catalyst (Fig. 5). The interpretation of the changes observed in the IR spectrum (Fig. 4b) is not straightforward, but it seems reasonable to assume that the cited losses may be tentatively attributed to the elimination of volatile iodinated metal complexes.

Finally, the thermal decomposition of SDT/$Rh_2Cl_2(CO)_4$: 5.1% wt/wt is reported in Fig. 6. Increasing the temperature up to over 300°C under an inert atmosphere leads to striking differences in terms of mass losses relative to SDT/$Rh_2Cl_2(CO)_4$. The almost linear loss of mass (Fig. 6a) can be related to the changes observed in the IR spectra. Indeed, while the chain backbone is relatively unaffected, a marked decrease is observed for the main band at 1969 cm^{-1} assigned to a Rh(I)-carbon monoxide species [8] while the contribution due to v(CO) bridging carbonyl groups at 1824 cm^{-1} [9] almost disappears (Fig. 7a and b). In agreement with the observations reported above, even in this case the mass losses are barely percetible under isothermal conditions (Fig. 6b) at 180°C and no Rh(I)→Rh(III) conversion is detected (Fig. 7c). By iodomethylating SDT/$Rh_4(CO)_{12}$, an additional band at 2048 cm^{-1} assigned to a Rh(III)-carbon monoxide species becomes more evident with respect to the previous catalyst (Fig. 8a relative to Fig. 4a) suggesting a more pronounced interaction with CH_3I. Once again, however, on heating (Fig. 9) the absorptions of Rh(I) and Rh(III)

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* It is known that this interaction is fundamental from a mechanistic point of view in the Monsanto process which leads to acetic acid through the rhodium catalyzed methanol carbonylation.

complexes still present up to 200°C (Fig. 8) almost disappear over 300°C (Fig. 8c).

Conclusions

A novel rhodium-containing diphenylphosphinated copolymer of styrene and divinylbenzene used as catalyst for methanol carbonylation was shown to be stable up to 250°C.

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