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Support and precursor effects on the preparation of new heterogenized Pt/Sn catalysts for the selective hydroformylation of 1-pentene

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New heterogenized Pt/Sn catalysts selective for the hydroformylation of 1-pentene have been synthesized. The complex cis-[$PtCl_2(PPh_3)_2$] and the $SnCl_2 \cdot 2H_2O$ or SnC_2O_4 precursors have been anchored on silica-, magnesia- and alumina-carriers. X-ray photoelectron spectroscopy was used to determine the surface composition and the nature of the anchored species. The hydroformylation activity was found to depend on the type of support and tin precursor used. Only the silica supported catalysts were active in the hydroformylation reaction. Samples prepared from $SnCl_2 \cdot 2H_2O$ were 200-fold more active than those prepared from SnC_2O_4. Selectivity to *n*-hexanal of the silica-supported catalyst prepared from $SnCl_2 \cdot 2H_2O$ was as high as 94.4% at 39.2% conversion of 1-pentene.

Keywords: Oxide-supported Pt/Sn catalysts; hydroformylation on supported Pt/Sn complexes; homogeneous–heterogeneous catalysis

1. Introduction

In recent years many studies have been carried out on the use of Pt/Sn systems as catalysts in the olefin hydroformylation reaction [1–4]. Systems based on platinum complexes and $SnCl_2$, both in homogeneous phase as well as polymer-supported, have shown high activities and regioselectivities in the field of asymmetric hydroformylation [5–7]. However, the use of homogeneous or polymer-supported catalysts leads to numerous practical problems, e.g., corrosion, difficulty of catalyst recovery, thermal stability etc. [8–10]. These problems could be overcome by anchoring the organometallic complexes to the surface of an inorganic oxide.

In this work we have studied the preparation of new heterogenized Pt/Sn catalysts from cis-[$PtCl_2(PPh_3)_2$] and $SnCl_2 \cdot 2H_2O$ or SnC_2O_4 on silica, alumina and magnesia supports. The hydroformylation of 1-pentene has been carried out on the catalysts and the effect of the precursor and support has been studied.

2. Experimental

The following supports were used: Degussa aerosil silica (200 m^2 g^{-1}), Girdler γ-alumina T-126 (188 m^2 g^{-1}) and magnesia (96 m^2 g^{-1}) obtained by thermal decomposition under vacuum of $Mg(OH)_2$.

Supports were impregnated with an ethanol solution of $SnCl_2 \cdot 2H_2O$ or an aqueous solution of SnC_2O_4; they were treated under high vacuum at 373 K for 16 h and then platinum was incorporated from a methylene chloride solution of cis-$[PtCl_2(PPh_3)_2]$. Finally, samples were dried under high vacuum for 16 h at 373 K. Resulting catalysts had a 1% weight platinum loading, and a Sn : Pt atomic ratio of 2 : 1.

For the infrared measurements self-supporting wafers of either the fresh or spent catalysts were prepared. The spectra were recorded with a Nicolet ZDX Fourier Transform instrument. X-ray photoelectron spectra (XPS) of the fresh preparations were recorded on a Leybold LHS 10 electron spectrometer provided with a Mg K_α excitation source ($h\nu = 1253.6$ eV) and a hemispherical electron analyser. Although surface charging was observed for all samples accurate (± 0.2 eV) binding energies (BE) could be determined by charge referencing with the Si 2p, Al 2p or Mg 2p peaks.

Hydroformylation of 1-pentene was performed in a Berghof 100 ml teflon-coated magnetically stirred stainless-steel autoclave at 373 K and 80 bar total pressure ($P_{CO} = P_{H_2}$). The olefin/Pt ratio used was 2000/1 and no solvent was added. After the reaction, products were analysed by gas chromatography using a Hewlett-Packard 5890 A instrument equipped with a 50 m HP-Ultra 2 capillary column.

3. Results and discussion

The anchoring of the cis-$[PtCl_2(PPh_3)_2]$ to the tin impregnated supports was followed by infrared spectroscopy. The resulting samples were found to be stable both under vacuum (10^{-6} Torr) and under hydrogen (400 Torr) up to 423 K. Platinum found in the post-reaction solution was similar for all samples, and lower than 5% (w/w) of initial platinum loaded in the catalyst. Tin was not detected in any case.

The chemical state and the relative abundance of the active components Pt and Sn have been revealed by XPS. The relative abundance of these components at the catalyst surface has been determined from the intensity of the

Table 1
Electron binding energies (eV) in core atomic levels and surface atomic ratios obtained from XPS for the Pt/Sn catalysts

Catalyst	Sn 3d$_{5/2}$	Pt 4f$_{7/2}$	Sn/M [a]	Sn/Pt
Pt/SnC_2O_4/silica	487.1	68.7	0.0079	8.1
Pt/$SnCl_2$/silica	486.7	68.8	0.0048	4.3
Pt/SnC_2O_4/magnesia	487.0	69.9	0.0008	0.1
Pt/$SnCl_2$/magnesia	487.2	69.7	0.0008	0.1
Pt/SnC_2O_4/alumina	487.1	71.7	0.0130	8.8
Pt/$SnCl_2$/alumina	486.5	70.1	0.0213	4.7

[a] M = Si, Mg, Al.

Sn 3d, Pt 4f, Al 2p, Si 2p and Mg 2p peaks, averaged for the number of scans, and published atomic sensitivity factors [11]. The XPS results are summarized in table 1.

For all catalysts the BE values for Sn 3d$_{5/2}$ core level electrons indicate the presence of oxidized tin species mainly as Sn(II). For silica and magnesia supports the BE values of the Pt 4f$_{7/2}$ core level electrons did not depend on the tin precursor used, but they did depend on the support. However, for the alumina supported samples the BE values of the Pt 4f$_{7/2}$ core level electrons depended on the tin precursor used. These findings indicate that both the support and the tin precursor determine the electronic interaction between the platinum precursor complex and the surface of the tin-modified support. Silica samples showed the lowest Pt 4f$_{7/2}$ BE values corresponding to reduced platinum species on the surface. Magnesia-supported samples showed the best-resolved line profiles and the narrowest peak-widths for the Sn 3d levels. This would indicate a homogeneous interaction between tin and the magnesia support, very likely through the same type of surface OH groups. It can also be noted in table 1 that magnesia-supported samples display the lowest Sn/M (M = Mg) and Sn/Pt ratios. As the analysis depth of XPS is confined to ≈ 2 nm, these facts would indicate that the anchorage of the tin species to magnesia surface mainly occurs inside the narrow pores of the carrier which have been developed during its thermal activation. These findings could be related with the absence of catalytic activity in the hydroformylation reaction observed for these catalysts under our experimental conditions. Alumina- and silica-supported catalysts presented a similar Sn/Pt surface ratio for a given tin precursor (see table 1). For the Pt/SnC_2O_4/silica and Pt/SnC_2O_4/alumina samples, substantial segregation of tin species on surface was established. The Sn/Pt ratio found for the most active catalyst, Pt/$SnCl_2$/silica, was very close to that generally used with the system cis-[$PtCl_2(PPh_3)_2$]/$SnCl_2$ in homogeneous phase. However, the Pt/$SnCl_2$/alumina sample, with a similar Sn/Pt surface ratio presented negligible activity in the hydroformylation reaction. Thus, the catalytic

Table 2
1-pentene hydroformylation results for silica-supported catalysts. (Reaction time 6 h, $P_{total} = 80$ bar, $P_{CO} = P_{H_2}$, $T = 373$ K, Pt/olefin = 1/2000)

Catalyst	Olefin conversion (%)	Selectivity (% *n*-hexanal)	TOF [a]
Pt/SnC_2O_4/silica	0.2	60	0.5
$Pt/SnCl_2$/silica	39.2	94.4	108
$Pt/SnCl_2$/silica [b]	8.5	95.5	28

[a] In mol aldehyde $mol^{-1}Pt\ h^{-1}$.
[b] Run at 343 K.

activity was determined not only by this Sn/Pt surface ratio but also by the support used.

The results concerning catalytic activity in the hydroformylation of 1-pentene for the silica-supported samples are shown in table 2. Only C_6-aldehydes (*n*-hexanal and 2-methyl-pentanal) were observed as reaction products. When the reaction time was extended to 24 h, the linear-to-branched C_6-aldehydes ratio was unchanged, but heavier products appeared, probably resulting from aldolic condensation. Silica-supported catalysts prepared from $SnCl_2$ showed the highest activity and selectivity to linear aldehyde. Thus, catalytic behaviour was highly dependent on the tin precursor used in the preparation of the catalysts.

After reaction, a carbonyl species with $\nu(CO) = 2045\ cm^{-1}$ and an acyl species with $\nu(CO) = 1690\ cm^{-1}$ were determined by infrared spectroscopy on the silica-supported catalyst: $Pt/SnCl_2$/silica. This behaviour is very close to the analogous homogeneous systems, where acyl species $[PtCl(COR)(PPh_3)_2]$ and $[Pt(SnCl_3)(COR)(PPh_3)_2]$ have been recovered after reaction under similar conditions [12,13]. The foregoing suggests that the anchored catalytic species proceed via similar homogeneous acyl complexes as intermediate species to the formation of aldehydes.

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