Organometallic complexes as a new type of heterogeneous catalysts in gas-phase

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Organometallic complexes are known to act as efficient homogeneous catalysts in numerous reactions[i,ii]. These soluble complexes are normally used in liquid phase in the presence of excess ligands. Homogeneous catalysts are basically molecular species, implying that the structure of the catalytic sites and thus also the catalytic properties are well defined in principle, which is the main advantage of homogeneous catalysis over heterogeneous catalysis.

Extensive research has been performed and is still being performed to combine the advantages of homogeneous catalysis and heterogeneous catalysis by immobilizing homogeneous catalysts on solids. A recent review by Valkenberg and Hölderich[iii] gives an excellent description of the state of the art. The most common approach is the heterogenization of organometallic compounds by attaching the complexes on inorganic or organic supporting material. Quite a number of strategies have been developed to attach complexes to solids, e.g. covalent anchoring, electrostatic adsorption, ship-in-a-bottle and supported liquid phase. However, in many cases these systems are not sufficient stable; leaching of both the metal as well as insufficient bonding between the ligands and the support are general problems that have not been solved in most cases.

In this work we demonstrate the principle of using solid organometallic complexes as a catalyst in gas-phase; leaching is evidently impossible in the absence of a liquid phase. Reactants and products need to be reasonably volatile and the temperature of operation is therefore higher then usual for homogeneous catalysis. Therefore, the complexes of choice are more thermally stable than averaged homogeneous catalysts. The relatively high temperature applied allows the use of compounds with a lower intrinsic activity.

We have chosen the hydroformylation (HF) of ethene, because activity of the catalyst for either HF or hydrogenation can be easily detected. The usual HF catalysts $HRh(CO)(PR_3)_3$ and $HCo(CO)_4$ are not stable under these harsh conditions. The well known Wilkinson catalyst is however capable of gas phase hydroformylation of ethane (table 1).

Table 1: Effect of metallic Rh vs Rh complex for the hydroformylation of ethylene.

Catalyst	**Activity (x 10^{-7} mol/g(cat).s)**	
	Ethane	**Propionaldehyde**
$RhCl(P(C_6H_5)_3)_3$	<0.01	2.3
Rh*	14.7	16.2

Conditions: Catalyst loading: 1.5 g; Flow rate 25 ml/min; Pressure: 7.7 bar; Reaction temperature: 200°C. * Decomposed under reaction mixture (1:1:1 $CO/H_2/C_2H_4$) at 350°C for 2h.

The activity of the Wilkinson catalyst is less than the activity of metallic Rh formed via decomposition of the complex. However, the HF/hydrogenation ratio of the Wilkinson catalyst is much better.

The interaction of the Wilkinson catalyst with gaseous CO has been studied with TGA, *in-situ* IR spectroscopy, elemental analysis with XRF and with NMR. It is concluded that the Wilkinson complex is converted according to:

$RhCl(P(C_6H_5)_3)_3 + CO \rightarrow RhCl(CO)(P(C_6H_5)_3)_2 + P(C_6H_5)_3$

Characterization of spent catalyst with IR spectroscopy (Figure 1) as well as elemental analysis with XRF, revealed that the CO-containing complex is most likely the actual active phase in the catalytic experiments.

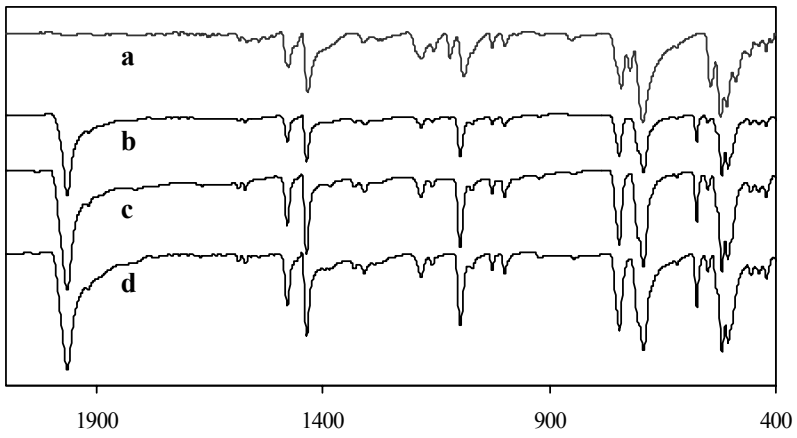

Fig. 1. FTIR spectra of (a) $RhCl(P(C_6H_5)_3)_3$ (b) $RhCl(CO)(P(C_6H_5)_3)_2$ (c) $RhCl(P(C_6H_5)_3)_3$ exposed to CO at 200°C (d) spent catalyst after hydroformylation reaction for 11 days.

Comment: Plaatje vervangen met detail pieken waaruit de gelijkenis-verschillen duidelijk blijken

In the temperature window up to 200°C hydroformylation is the predominant reaction and metallic Rh is not formed. Decomposition of the complex under reaction conditions is observed at temperatures well above 200 °C. Also after decomposition, the formation of metallic Rh is accompanied by a shift in selectivity from hydroformylation towards hydrogenation.
We conclude that organometallic complexes can perform as heterogeneous catalysts in gas phase. This indicates that new heterogeneous catalysts may be developed based on thermally stable organometallic complexes.

[i] B. Cornils, W. A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, Vols 1-2, VCH, Weinheim, Germany (1996)
[ii] R. Noyori (Ed.), Asymmetric Catalysis in Organic Synthesis, John Wiley and Sons, Inc., New York (1994)
[iii] M.H.Valkenber and W.F. Hölderich, Catal. Reviews, 44 (2002) 321-374