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Gas phase hydroformylation of ethylene using organometalic Rh-complexes as heterogeneous catalysts

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The heterogeneously catalysed gas phase hydroformylation of ethylene to propionaldehyde was studied over solid $RhCl(PPh_3)_3$ and $RhCl(CO)(PPh_3)_2$. At 3 bar and 185 °C, an active phase formed from $RhCl(PPh_3)_3$ which was different from $RhCl(CO)(PPh_3)_2$ under the reaction conditions studied. The selectivity of $RhCl(PPh_3)_3$ to propanal was much better than that of supported Rh-metal. Thus, solid metal-complexes operated in gas phase reactions clearly hold promise as a new class of heterogeneous catalysts.

KEY WORDS: ethylene hydroformylation; rhodium complex; gas phase heterogeneous catalysis; Wilkinson's catalyst.

1. Introduction

Organometallic compounds and other metal-complexes are known to be efficient homogeneous catalysts in numerous liquid phase reactions [1–3]. The main advantage of homogeneous catalysts compared to heterogeneous ones is the fact that catalytic properties can easier be tuned since the structure of the active species is better defined. However, in many applications, the separation of homogeneous catalysts from reactants and products is the most important drawback. Significant investments are often necessary to separate and re-use the catalyst and, moreover, decomposition of the catalyst and/or the ligands is frequently a key problem, especially when high temperatures are encountered in distillation sections.

As a result, extensive research has been carried out to combine the advantages of homogeneous and heterogeneous catalysts by immobilizing homogeneous catalysts on solid supports. A recent review by Valkenberg and Hölderich [4] gives an excellent description of the state of the art. Unfortunately, in many cases these systems are not sufficiently stable; leaching of the metal-complexes as a result of insufficient bonding between ligands and support are general problems that have not been solved in most cases [5].

This paper describes an alternative approach to solve these problems, namely to apply organometallic complexes directly as a heterogeneous catalyst: operate the solid metal-complex in a gas-phase reaction, i.e. all reactants and products are in the gas-phase while the catalyst is solid. As such leaching is avoided by preventing the presence of any liquid phase. Obviously, this approach is only possible as long as condensation temperatures of reactants and products are not too high. In addition, the complex needs to be sufficient stable under the applied reaction conditions.

To investigate the feasibility of this method we chose the hydroformylation of ethylene to propionaldehyde as a test reaction, with hydrogenation to ethane as the only parallel reaction that can occur. Since Rh is known to be active in hydroformylation, bulk $RhCl(PPh_3)_3$, often called Wilkinson's Catalyst [6, 7] was selected as a catalyst because of its well known stability.

2. Experimental

2.1. Chemicals

Hydrogen, carbon monoxide and ethylene were purchased from PraxAir, Inc. with a purity of 99.5% and were employed without further purification. A gas mixture of $H_2/CO/C_2H_4$ (1:1:1) was used for the catalytic experiments (PraxAir, Inc., composition: H_2: 33.2 ± 2 vol.%, CO: 33.4 ± 2 vol.%, C_2H_4: 33.2 ± 2 vol.%). $RhCl(PPh_3)_3$ was purchased from Alfa-Aesar chemicals with a purity of 99.99% and was used without further purification. $RhCl(CO)(PPh_3)_2$ was purchased from Strem Chemicals with purity of 99.0% and was used without further purification.

2.2. Catalyst characterisation

DRIFT spectra were recorded using a Fourier transform infrared spectrometer (NICOLET 20 XSB FT-IR). *Ex-situ* experiments were performed to characterize the spent catalyst. Elemental analysis was done with a Philips PW1480 XRF spectrometer (Rh, Cl, P) and a Fisons AAS instrument EA1108 (C,H).

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2.3. Catalytic testing

The hydroformylation reaction was conducted in a U-shaped fix bed flow reactor of stainless steel with a inner diameter of 4.6 mm. 0.4 g of solid complex was packed in the reactor and fixed with quartz wool plugs. The reactor was placed in an oil bath to regulate the temperature. Reaction pressure was controlled between 1 and 3 bar with a backpressure regulator. Before reaction, the system was purged at 50 °C with N_2 (12 mL/min) for 5 min and subsequently with the reaction mixture (gas mixture (33% CO, 33% H_2, 33% C_2H_4)/N_2 = 6/1) for another 5 min. The gas composition of reactants and products were on-line analyzed with a gas chromatograph (Varian 3600) equipped with analytical columns Molsieve (2.0 m × 1/4 inch) and HayeSep (2.5 m × 1/4 inch).

3. Results

3.1. Catalytic testing

Figure 1 shows the reaction rate over $RhCl(PPh_3)_3$ towards propanal and ethane at 185 °C and 1 bar (a) or 3 bar (b). For both pressures, initially a high ethane formation rate is found, which decreases in the first 2 h of reaction. After 450 min at 1 bar (figure 1a), ethane and propanal formation rates are low, with only 30% selectivity to hydroformylation. Total initial activity was about two orders of magnitude higher at 3 bar compared to 1 bar. Moreover, at 3 bar, an increase in propanal formation rate was observed after 2 h of reaction. After 450 min it stabilized and resulted in 76% selectivity for hydroformylation. After 450 min, the propanal formation rate was approximately 50 times higher at 3 bar than at 1 bar.

To test the possible formation of metallic Rh during these experiments, Wilkinson's catalyst was decomposed at 245 °C for 3 h in flowing nitrogen. Subsequently, the reactor was cooled to 185 °C and reaction was performed at 3 bar. It was observed that the overall activity of the catalyst increased about ten times compared to the measurements at 3 bar and 185 °C without decomposition. However, at the same time, selectivity collapsed to about 44% propanal.

Since it is well-known in homogeneous catalysis that during reaction with Wilkinson's catalyst, substitution of PPh_3 occurs by CO, solid $RhCl(CO)(PPh_3)_2$ was tested as a reference compound under the same reaction conditions (figure 2). At 1 bar, the propanal formation rate after 2 h of reaction is comparable to that of Wilkinson's catalyst (figure 1a), but over $RhCl(CO)(PPh_3)_2$ clearly a higher hydrogenation rate occurs. At 3 bar, $RhCl(CO)(PPh_3)_2$ exhibits a comparable total activity but a much lower selectivity (only 38%) to propanal than was observed over $RhCl(PPh_3)_3$. In addition, $RhCl(CO)(PPh_3)_2$ did not show a strong deactivation in the first hours of reaction in contrast to $RhCl(PPh_3)_3$.

Table 1 summarizes the observed activity and selectivity for $RhCl(PPh_3)_3$, decomposed $RhCl(PPh_3)_3$, and $RhCl(CO)(PPh_3)_2$ after 600 min time-on-stream.

3.2. Catalyst characterisation

3.2.1. Elemental analysis

Table 2 shows the elemental composition of the fresh metal complexes and the used Wilkonson's catalyst. The elemental composition of the spent catalyst was found to be in between the composition of $RhCl(PPh_3)_3$ and $RhCl(CO)(PPh_3)_2$ with respect to the Rh:P ratio while the Rh:Cl ratio was comparable.

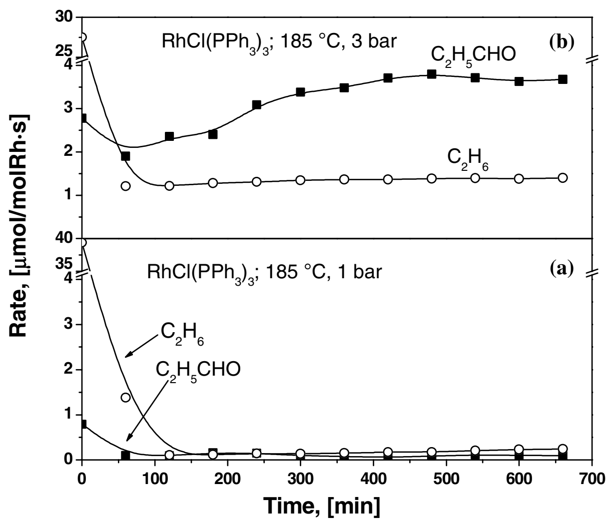

Figure 1. Propanal and ethane formation rates of with time-on-stream over 0.4 g $RhCl(PPh_3)_3$ powder at 185 °C, gas flow rate 3.5 ml/min (a) at 1 bar (b) at 3 bar.

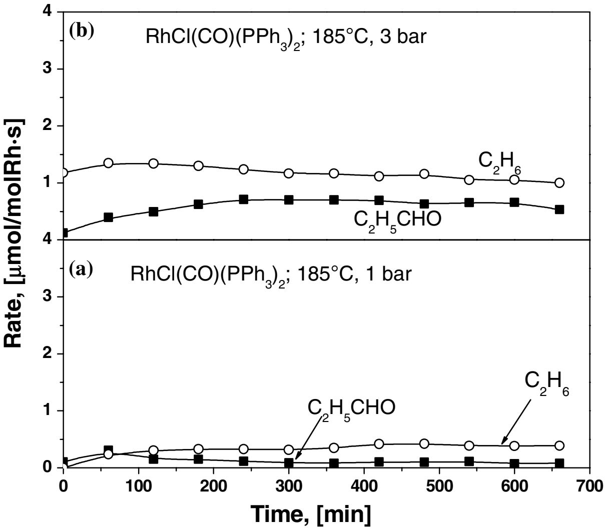

Figure 2. Propanal and ethane formation rates with time-on-stream over 0.4 g $RhCl(CO)(PPh_3)_2$ powder at 185 °C, gas flow rate 3.5 ml/min. (a) at 1 bar, (b) at 3 bar.

Table 1
Rates and selectivity to propanal and ethane over $RhCl(PPh_3)_3$, decomposed $RhCl(PPh_3)_3$, and $RhCl(CO)(PPh_3)_2$ after 600 min time-on-stream at different reactions conditions

Catalyst Reaction conditions	Propanal formation rate (μmol mol Rh^{-1} s^{-1}) (after 600 min)	Propanal selectivity (after 600 min)
$RhCl(PPh_3)_3$		
185 °C, 1 bar	0.03	0.30
185 °C, 3 bar	0.96	0.76
$RhCl(CO)(PPh_3)_2$		
185 °C, 1 bar	0.03	0.16
185 °C, 3 bar	0.24	0.38
Decomposed $RhCl(PPh_3)_3$		
185 °C, 3 bar	3.79	0.44

3.2.2. *DRIFT-spectroscopy*

The spent catalyst was characterized by *ex-situ* FT-IR spectroscopy. Figure 3 displays the characteristic areas from the DRIFT spectra of fresh $RhCl(PPh_3)_3$ and $RhCl(CO)(PPh_3)_2$, and the spent $RhCl(PPh_3)_3$-catalyst obtained after the experiment at 3 bar and 185 °C as described above. Figure 3 shows that the spent catalyst (top, grey line) has developed clearly new bands at 575, 1098, 1918, and 1963 cm^{-1} compared to the fresh Wilkinson catalyst (bottom, black line). The new bands at 1918 and 1963 cm^{-1} can be assigned to C–O stretch vibrations of CO coordinated to Rh. In addition at 575 cm^{-1}, the Rh–C–O bending vibration is clearly observed at the same position as it is found for fresh $RhCl(CO)(PPh_3)_2$ [8]. Interestingly, C–O stretch vibrations in $RhCl(CO)(PPh_3)_2$ were found at two positions: 1975 and 1958 cm^{-1}, while for the spent catalyst only one intense peak at 1963 cm^{-1} was observed. The broad peaks from 1850–2050 cm^{-1} visible in the spectrum of fresh $RhCl(PPh_3)_3$ are due to the overtones of the phenyl groups [9]. Between 1050 and 1150 cm^{-1} P–C stretch vibrations and C–H vibrations of the PPh_3 groups are located [10]. Here it can be seen that the spent catalyst shows features of both the fresh Wilkinson catalyst and $RhCl(CO)(PPh_3)_2$.

4. Discussion

The turn-over-Frequency (TOF) and selectivity to propanal for $RhCl(PPh_3)_3$ and $RhCl(CO)(PPh_3)_2$ after 600 min time-on-stream at different reactions conditions are given in table 1. At 1 bar and 185 °C both samples have a negligible activity for hydroformylation. However at 3 bar, it is evident that Wilkinson's catalyst exhibits a fairly high hydroformylation rate after 600 min, despite the initial high hydrogenation rate (figure 1). Propanal formation rate was 0.96 μmol propanal/(mol Rh s) with a selectivity of 76% after 600 min time-on-stream at 3 bar and 185 °C. Contribution of metallic Rh particles under the applied conditions can be ruled out, since the selectivity to propanal of the decomposed catalyst was only half of that of the Wilkinson complex (table 1). Furthermore, under the same conditions $RhCl(CO)(PPh_3)_2$ showed four times lower activity towards propanal, and also propanal selectivity was much lower (38%).

Comparison of the activity and selectivity of $RhCl(PPh_3)_3$ and $RhCl(CO)(PPh_3)_2$ (table 1) shows that the active phase formed from $RhCl(PPh_3)_3$ under reaction conditions is different from the active phase formed from $RhCl(CO)(PPh_3)_2$. Moreover, *ex-situ* characterization by DRIFT (figure 3) and elemental analysis (table 2) of the spent catalyst also indicated that the initial $RhCl(PPh_3)_3$ was not converted into $RhCl(CO)(PPh_3)_2$. From DRIFT, it is clear that CO added to the initial Rh-complex, but its stretch vibration is not in the same position as for $RhCl(CO)(PPh_3)_2$. Further, the characteristic PPh_3 vibrations (1050–1150 cm^{-1}) seem to be a mixture of the vibrations from both $RhCl(PPh_3)_3$ and $RhCl(CO)(PPh_3)_2$. Elemental analysis of the spent catalyst (table 2) also confirms this observation when comparing phosphor and carbon amounts. These data seem to be in contrast with

Table 2
Elemental analysis of fresh $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, and spent $RhCl(PPh_3)_3$ (185 °C, 3 bar)

	$RhCl(PPh_3)_3$	$RhCl(CO)(PPh_3)_2$	Spent catalyst
Rh (wt.%)	11.17	15.86	11.69
Cl (wt.%)	3.67	5.10	3.90
P (wt.%)	10.88	9.35	10.05
H (wt.%)	4.81	4.11	4.53
C (wt.%)	70.30	64.64	68.99
SiO_2*			0.85
Cl/Rh molar ratio	0.95	0.93	0.97
P/Rh molar ratio	3.24	1.96	2.86
C/P molar ratio	16.7	17.8	17.7

*Quartz wool was used during the catalytic experiment.

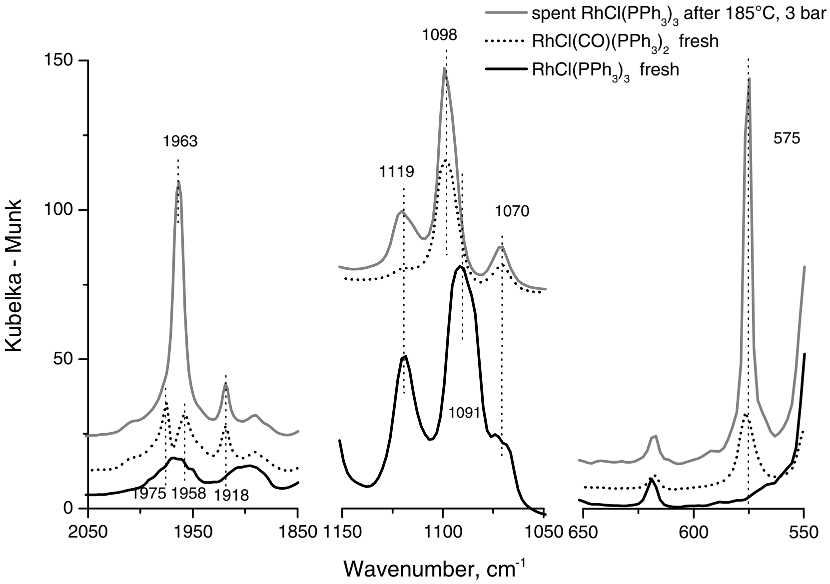

Figure 3. *Ex-situ* DRIFT spectra of fresh $RhCl(PPh_3)_3$ (bottom, black line); fresh $RhCl(CO)(PPh_3)_2$ (middle, dotted line); spent $RhCl(PPh_3)_3$ used at 185 °C and 3 bar (top, grey line).

Robinson *et al.* [11], who reported that supported $RhCl(CO)(PPh_3)_2$ can be used as a stable catalyst for hydroformylation of propylene at temperatures up to 225 °C. However, these authors worked with supported catalysts at much higher pressures (49 bar) and used propylene instead of ethylene. No data were reported for ethylene hydroformylation at 1–3 bar using $RhCl(CO)(PPh_3)_2$. Further *in-situ* investigations are presently being performed to reveal the exact structure and composition of the active hydroformylation phase.

To assess the possibility of application of bulk organometallic compounds in gas-phase reactions, the activity and selectivity found in this study is compared with data published in literature. For supported Rh-metal catalysts TOF's were reported of 3.85×10^3 μmol/(mol Rh s) for gas phase ethylene hydroformylation at 180 °C and 20 bar [12], and about 2.1 μmol/(mol Rh s) for propene hydroformylation at atmospheric pressure [13]. The latter study also reported that hydrogenation and hydroformylation proceeded with roughly equal rates at atmospheric pressure, which is in agreement with our results obtained on the decomposed catalyst (table 1). Immobilized homogeneous catalysts operated in liquid phase are in many cases more active. Typical rates of 5.3×10^4 μmol/(mol Rh s) can be estimated from the data of Yoneda *et al.* [14] for hydroformylation of propylene at 120 °C and 30 bar pressure using Rh immobilized on polymers. Industrial application of Rh, with excess triphenylphosphine (PPh_3) for propylene hydroformylation, results in typical 10^6 μmol/mol Rh s at 90 °C and 20 bar [15].

The activity values obtained in the present study for gas phase hydroformylation are clearly much lower, which can be explained by the lower pressures applied and a poor dispersion of the Wilkinson complex. Homogeneous catalysts and immobilized complexes operated in liquid phase are much more active, because the Rh complexes are much better dispersed in these catalysts compared to the solid 100 micron particles in the present study. It is obvious that only a very small fraction of the compound is located on the surface of these particles. Nevertheless, our catalyst performs much better than supported Rh metallic catalysts with respect to propanal selectivity (76% in our case). It thus clearly demonstrates that solid metal-complexes are a promising option to develop a new class of heterogeneous catalysts for gas-phase reactions.

5. Conclusion

$RhCl(PPh_3)_3$ powder is a precursor of a catalyst that is formed *in-situ* at 3 bar and 185 °C exhibiting high selectivity for ethylene hydroformylation. Although the overall activity of the catalyst, defined as rate per Rh-atom, is lower than the activity of a supported Rh-metal catalyst, the selectivity to hydroformylation is much better. Further, the activity is lower compared to homogeneous catalysts as well as immobilized catalysts operated in solvents, which can be easily explained by the low dispersion of the powders and the low pressures used in this study. Even so, solid metal-complexes operated in gas phase reactions clearly hold promise as a new class of heterogeneous catalysts.

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