

Hydroformylation of 1-Hexene with Supported Liquid Phase Catalyst (SLPC) $\text{RhHCO}(\text{P}\phi_3)_3$

The potential advantages of homogeneous catalysis over heterogeneous catalysis of the same reaction are the greater selectivity, the more efficient use of the catalyst atoms, and the easy control of the reaction temperature. The disadvantages of homogeneous catalysis are the difficulty of removing the products continuously and recovering the catalyst. To overcome these two problems Acres *et al.* (1) and Rony (2) independently suggested combining the desirable features of both systems by using a solution of the homogeneous catalyst, dissolved in a high boiling solvent, supported on a suitable carrier and employing the supported liquid phase catalyst (SLPC) in a fixed-bed gas reactor. Such catalysts are very convenient for a fast laboratory screening of catalyst systems. However, there is also a handicap in using the SLPC in gas-phase reaction as the contact time of the reactants with the catalyst is short (seconds up to minutes) while in solvent reactions the contact time of a homogeneous catalyst is practically unlimited. Therefore a supported liquid phase homogeneous catalyst must exhibit a very high activity or turnover (turnover = moles products/moles catalyst · time) to obtain a good space-time yield (kg product/volume · time).

Recently we have shown that under relatively mild conditions of pressure (1-15 bar) and temperature ($T \sim 50-200^\circ\text{C}$) in bulk reactions homogeneous hydrogenation and hydroformylation catalysts can be by a proper choice of the central atom and the ligands be developed to high turnovers, comparable to the turnovers of very good heterogeneous catalysts (3-6). In the bulk hydroformylation of 1-hexene with $\text{RhHCO}(\text{P}\phi_3)_3$ at 120°C , the ratio of n/i aldehyde was about 12, mean turnover 120

during 95 hr, and turnover number 700,000 (moles product/moles catalyst) (6).

Therefore we have tried this catalyst in the supported liquid-phase catalysis of the gas-phase hydroformylation of 1-hexene.

The catalyst preparation for the SLPC was as follows: 146 mg of $\text{RhHCO}(\text{P}\phi_3)_3$ (7) and 3.0 g of $\text{P}\phi_3$ were dissolved in 7.5 ml of CHCl_3 , 10 g Chromosorb (PAW-DMCS, 80-120 mesh, Riedel de Haen) added, the suspension stirred for 5 min (all operations under N_2), and the CHCl_3 drawn off in a flash-evaporator at 25°C under vacuum. The prepared, dry carrier was filled into a steel-column of 3 m length and 0.2 cm inner diameter (about 2 g carrier per 1 m column).

As reaction oven we used a Varian Aerograph 912 with heat conductivity detector. The products were trapped with liquid nitrogen. 1-Hexene was continuously injected with a "syringe-pump" into the injector ($T = 250^\circ\text{C}$) of the Aerograph. The carrier-gas was a mixture of $\text{CO}/\text{H}_2 = 1:1$, pressure was 2 bar, and the flow rate was in all experiments 60 ml gas/min (N.T.P.). The products were analyzed in another Aerograph with the following columns: Apiezon ($T = 120^\circ\text{C}$) for n - and i -aldehyde, Carbowax 1500 ($T = 25^\circ\text{C}$) for hexane and the hexenes, and capillary columns for the separation of the 2-*cis*, 2-*trans* and 3-*cis-trans* hexenes.

The results are given in Table 1, which shows the experimental data for the loading, injection time, temperature, conversion, and mole percent of the products for individual runs. Lowering the temperature increases the ratio n/i -aldehyde and decreases the isomerization of 1-hexene to 2-hexene (runs No. 1-7). The loading of the column from 14 to 84 $\mu\text{l}/\text{min}$ has practically no influence on the ratio of n/i (runs No. 8-10). The same holds for the injection time

TABLE 1

Summary of Loading ($\mu\text{l}/\text{min}$), Injection Time t (min), Temperature ($^{\circ}\text{C}$), Mole Percent Conversion, and Product Composition Data of 1-Hexene Hydroformylation in the Gas-Phase with SLPC^a

Run number	Loading ($\mu\text{l}/\text{min}$)	Injection time t (min)	T ($^{\circ}\text{C}$)	Conversion (%)	Mole percent of product				
					1-Hexene	2-Hexene	<i>n</i> -al	<i>i</i> -al	<i>n/i</i>
1	14	120	160	90	10	35	48.4	6.6	7.3
2	14	120	140	95	5	26	64.2	4.8	13.4
3	14	120	120	91	9	12	73.5	5.5	13.4
4	14	120	100	55	45	5	48.5	1.5	32.3
5	14	120	90	53	47	5	47	1	47
6	14	120	80	34	64	4.7	28.5	0.8	35.6
7	14	120	70	22	78	3	18.5	0.5	37
8	14	120	120	94	6	15	73.5	5.5	13.4
9	28	120	120	91	9	12	73.5	5.5	13.4
10	84	120	120	88	11	10	73.5	5.5	13.4
11	84	120	120	88	11	10	73.5	5.5	13.4
12	84	30	120	88	12	10	73.3	4.7	15.6
13	14	2.880	100	53.2	44	7	48	1.8	26.7

^a Catalyst: 87.6 mg $\text{RhHCO}(\text{P}\phi_3)_3$ + 1.8 g $\text{P}\phi_3$ on 6 g Chromosorb. Column: 3 m length, 2 mm inner diameter, volume 9.4 ml.

(runs No. 11 and 12). In all experiments the ratio of *cis/trans* hexene was about 1 : 1, no 3-hexene could be detected, and the percentage of hexane was $<0.5\%$. The mean sojourn time of 1-hexene in the column was about 2 min. From run No. 10 the space-time yield calculates to 0.34 kg/liter · hr. The column was operated for 2 days without loss of catalyst activity (compare runs No. 4 and 13). In run No. 11 at $T = 100^{\circ}\text{C}$ the weight of the catalyst was 6.125 g before and 6.128 g after the run. No loss of triphenylphosphine was observed. No rhodium was detected by atomic absorption in the products.

These studies on the hydroformylation of 1-hexene in the gas-phase with the supported homogeneous catalyst $\text{RhHCO}(\text{P}\phi_3)_3$, dissolved in molten $\text{P}\phi_3$, have given the same high ratio of *n/i*-aldehyde as was found in the bulk hydroformylation (6). Gerritsen *et al.* (7) described the hydroformylation of ethene and propene with SLPC $\text{RhHCO}(\text{P}\phi_3)_3$ as a function of carrier, temperature, solvent, the ratio

olefin: H_2 :CO, and the ligand L in RhHCOL_3 . With catalyst $\text{RhHCO}(\text{P}\phi_3)_3$ at 90°C and a total pressure of 16 bar the selectivity of *n/i*-butanal was 8.96. We found at the same temperature, but with $p = 2$ bar, a ratio of *n/i*-heptanal = 47 (run No. 5). Lowering the pressure in the bulk hydroformylation also increases the ratio of *n/i*-heptanal (8). Interestingly we also found hydroformylation at the melting point of triphenylphosphine (80°C) and below (runs No. 6 and 7). The same effect was observed in the hydroformylation of ethene and propene between 65 and 120°C (7). The very active catalyst $\text{RhHCO}(\text{P}\phi_3)_3$ also acts as a supported solid phase catalyst. From these results this type of catalysis may become an alternative to the true heterogeneous gas phase catalysis if more "homogeneous" catalysts of high turnover are available.

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