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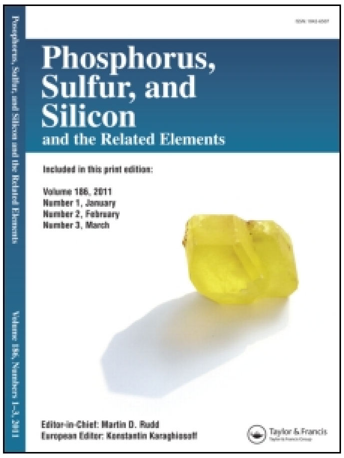

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Water-Soluble Phosphines as Ligands for Hydroformylation Catalysts

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WATER-SOLUBLE PHOSPHINES AS LIGANDS FOR HYDROFORMYLATION CATALYSTS

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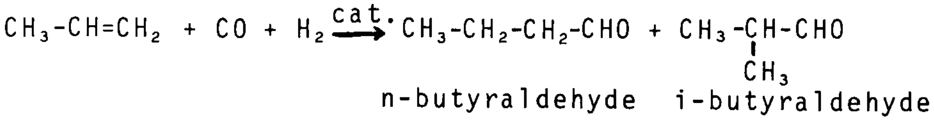
Abstract n-Butyraldehyde, the key intermediate in the manufacture of the most important plasticizer raw material, 2-ethylhexanol, is mainly obtained by the hydroformylation of propylene. In addition to the two established processes, the Co-high pressure and the Rh-low pressure process, Ruhrchemie and Rhône-Poulenc have developed a new variant using rhodium complexes as catalysts which are modified by water-soluble phosphines. As the catalyst phase is practically insoluble in the raw aldehyde, it can be separated from the catalyst by simple phase separation. The heat of reaction can be used for other purposes. The first commercial plant operating with this process has been in service at Ruhrchemie AG since mid-1984.

The use of water-soluble phosphines as ligands for hydroformylation catalysts is the latest variant of a synthesis which has been known for almost fifty years.

The hydroformylation reaction is the catalytic conversion of olefins with carbon monoxide and hydrogen, aldehydes being formed in an exothermic reaction. This is illustrated for propylene in the following equation:



$$CH_3\text{-}CH{=}CH_2 + CO + H_2 \xrightarrow{cat.} \underset{\text{n-butyraldehyde}}{CH_3\text{-}CH_2\text{-}CH_2\text{-}CHO} + \underset{\text{i-butyraldehyde}}{CH_3\text{-}\underset{CH_3}{\underset{|}{C}}H\text{-}CHO}$$

The most suitable catalyst metals are cobalt and rhodium which are employed homogeneously in the form of their hydridocarbonyl complexes. However, ligand modification, e.g. with triphenylphosphine is necessary, especially in the case of rhodium, which has become more and more popular for propylene hydroformylation, in order to combine its high activity with very good selectivity towards n-butyraldehyde and thus make its employment more economical.

The high price of rhodium necessitates the implementation of special engineering solutions to prevent losses of the precious metal and to separate the reaction products from the catalyst system with minimum impairment of the catalyst properties. The last of the requirements mentioned has proved to be problematic as the reaction products have to be thermally separated from the homogeneous catalyst system, i.e. by distillation. This operation not only consumes practically the entire heat of reaction but also impairs catalyst performance in time.

In view of these facts various tests were conducted in the past on the heterogenisation of hydroformylation catalysts. For example, the impregnation of carrier materials with rhodium complexes, the use of "polymer" phosphines as ligands, etc. The industrial application of such fixed-bed catalysts was doomed to failure as the rhodium leached out of the carrier material or similar problems occurred.

A breakthrough in the heterogenisation of hydroformylation catalysts was finally achieved in the laboratories of Rhône-Poulenc in France where water-soluble phosphines were used as complex ligands. This variant transfers the catalyst into a liquid phase which is practically immiscible with the raw aldehyde and which is then separated from the Oxo products by simple phase separation, i.e. without any energy being utilized, after the reaction has been completed. The catalyst solution can subsequently be returned to the reactor.

Water-soluble phosphines are obtained, for example, by the sulfonation of arylphosphines; triphenylphosphine is sulfonated to triphenylphosphine-trisulfonate (TPPTS) which can be employed, for example, as an alkali metal salt or ammonium salt.

The use of an alkali metal or an ammonium salt depends on the intended field of application. If lower olefins are to be converted, alkali metal salts are given preference, whereas it is better to take ammonium salts for higher olefins.

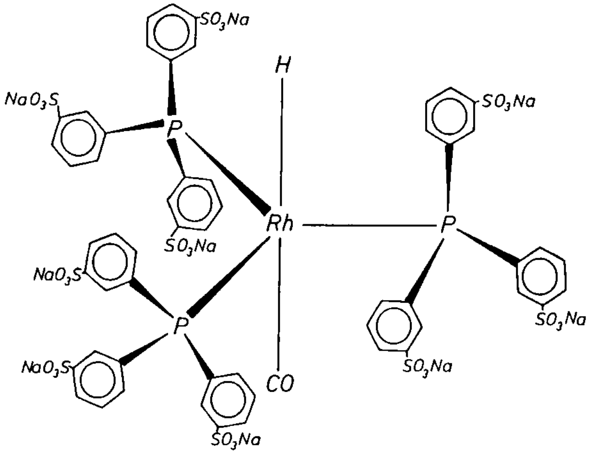


FIGURE 1 Catalyst of the RCH/RP-process

If rhodium hydroformylation catalysts are modified with water-soluble, sulfonated phosphines (fig. 1), the chemical advantages of the rhodium catalysts - high activity with excellent selectivity towards the straight-chained aldehyde - are combined with the engineering advantage of simple separability of the catalyst system from the raw aldehyde.

As this process variant promised economic advantages, is was developed to technical maturity in the technical departments of Ruhrchemie AG. The first commercial plant to work according to this new process with a capacity of 100,000 t/a n-butyraldehyde has now been in operation for more than two years. Fig. 2 shows the process flow sheet.

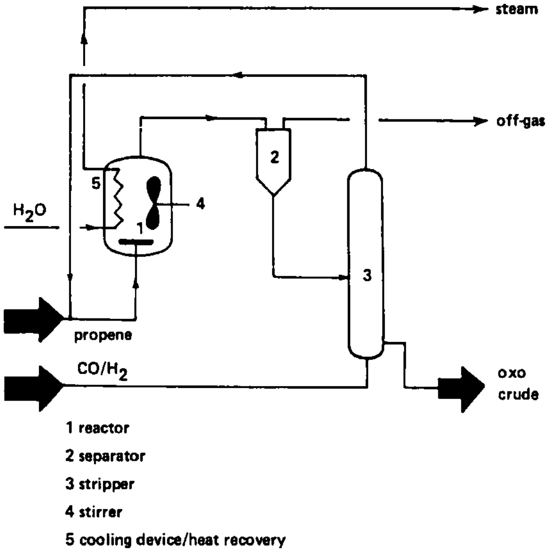


FIGURE 2 Flow sheet

The process advantages worked out in the laboratory and pilot plant tests were realized quantitatively. The fact that manufacture and handling of the catalyst ligand are unproblematic deserves particular mention.