

New Technology for Industrial Hydroformylation

RHODIUM-BASED CATALYST SYSTEM FOR OXO PROCESS PLANTS

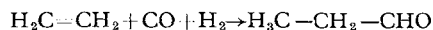
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New technology for the hydroformylation of olefins has been developed jointly by Union Carbide Corporation, Davy Powergas Limited and Johnson Matthey & Co. Limited. The process employs a novel rhodium-based homogeneous catalyst system at significantly lower pressures and temperatures than conventional cobalt-using processes, resulting in major savings in capital investment and operating costs. Another most important feature of the new process is that it provides much higher ratios of normal:iso aldehydes produced when propylene and other olefins are used as feedstocks than is possible with conventional processes. Several plants utilising the new system are now under construction.

The use of carbon monoxide in industrial organic chemistry is of fast growing importance. Much of the work on which this growth has been based was carried out within the last forty years. The crucial discovery of the hydroformylation or oxo reaction was made by Roelen of Ruhrchemie A.G. in 1938 and it is from his studies that the technology of hydroformylation has developed.

Hydroformylation is defined as the reaction of an unsaturated olefinic compound with hydrogen and carbon monoxide to yield an aldehyde. The original oxo reaction of Roelen showed that propionaldehyde was formed from ethylene:



and that diethylketone was also formed. However, ketone formation occurred to a large extent only with ethylene and consequently Adkins' term "hydroformylation" for this reaction is a better general description than "oxo". The reaction is exothermic—with propylene 30 kcal/mole is evolved. The heat evolved with other olefins varies between 28 and 35 kcal/mole depending on their structure and molecular weight.

In addition to olefins (alkenes) it would be possible to use as feedstocks for hydroformylation alkyl alkenoates, alkenyl alkanates, alkenyl alkyl ethers, and alkanols. Polymers, i.e. polyolefins, might also be reacted similarly.

One of the principal reasons for employing this technique of hydroformylation is that a second stage process using hydrogen can convert aldehydes from the standard hydroformylation process into the so-called oxo alcohols, which are of great industrial significance. Oxo products and their derivatives include such diverse chemicals as plasticisers, solvents, paint resins, and—more recently—bio-degradable detergent intermediates and lube oil additives.

Suitable Catalysts

The essential key to the hydroformylation reaction is the use of a suitable catalyst. Roelen originally employed the solid Fischer-Tropsch catalyst based on cobalt but it was subsequently discovered that the catalytic mechanism is homogeneous in nature. The process was therefore developed using homo-

geneous cobalt catalysts such as cobalt hydrocarbonyl $\text{HCo}(\text{CO})_4$. A number of mechanisms for the action of this catalyst were proposed and the influence of catalyst concentration on the variation in reaction products was established. In due course, however, it was found that modification of $\text{HCo}(\text{CO})_4$ by replacing one or more of the carbonyl ligands by other ligands was beneficial.

From theoretical considerations it became apparent that catalysts based on Group VIII metals other than cobalt might have application in the hydroformylation reaction. Rhodium and ruthenium both seemed to be promising candidates for study and work was undertaken on these platinum group metals. Of particular importance was the work carried out by Professor Geoffrey Wilkinson, F.R.S., at Imperial College, London, and also certain associated investigations carried out by staff at the Johnson Matthey Research Laboratories at Wembley and by Davy Powergas Limited at Stockton, Teesside.

Wilkinson introduced the concept of triphenylphosphine ligands substituted into rhodium hydrocarbonyl (analogous to cobalt hydrocarbonyl). His $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ homogeneous catalyst is well known. It has been claimed that this makes it possible to undertake reactions at temperatures as low as 25°C and at pressures as low as one atmosphere, while giving the very desirable ratio of *normal* to *iso*-aldehydes of about 20, a figure very much greater than in conventional processes based on the use of cobalt catalysts.

The superior thermal stability of modified hydrocarbonyls is explained by the fact of trivalent phosphorus ligands being better σ -donors than CO but poorer π -acceptors. Thus the remaining CO ligands are more strongly bonded, because the transition metal atom has the tendency to transfer the increased negative charge obtained from the phosphorus to the CO ligands through π -back donation.

Phosphine-modified catalysts possess greater stereoselectivity than unmodified hydrocarbonyl catalysts. Various arguments

have been put forward to account for this behaviour. However, isomerisation of the feedstock materials is almost completely suppressed when working with rhodium carbonyls and excess trialkylphosphines, giving virtually complete conversion to aldehydes.

An essential stage in any catalytic process is the separation and recovery of the catalyst. The ease and completeness of this operation is of great economic importance to oxo plant operators. In the case of homogeneous reactions where the feedstock, the catalyst and the reaction products all exist in the same medium it is particularly important to carry out the separation efficiently to arrive at both purity of reaction product and availability of the catalyst material for recycling.

New Technology

So far we have considered the principles of hydroformylation and have indicated some of the problems that have to be solved in developing a successful commercial operation of the process. The aim has been to eliminate the need to operate at very high operating pressures, and to increase the selectivity to obtain more of the desired normal-chain isomer products.

New technology that meets this aim has now been developed jointly by Union Carbide Corporation, Davy Powergas Limited and Johnson Matthey after work extending over more than seven years. The essence of this work lies in the development of a satisfactory rhodium-based catalyst, which permits olefins such as propylene or ethylene to be converted economically on a large production scale into *n*-butyraldehyde and propionaldehyde, respectively, in high yield and with great selectivity. The selectivity is stated to be 10:1 for *n*:*iso* butyraldehydes from propylene, for example. This means a saving of 20 per cent of propylene compared with what would be required in the production of *n*-butyraldehyde by conventional cobalt-using processes, where in general the *n*:*iso* ratio is only 3:1. It is possible that a

saving of \$6,000,000 per year on propylene plus synthesis gas ($\text{CO} + \text{H}_2$) feedstock may be achieved on a large commercial plant. Previously it has been necessary to recycle the unwanted *iso*-butyraldehyde, for example as fuel, and pressures of around 300 atmospheres have had to be used with the cobalt catalysts.

The new process technology possesses other advantages. The relatively low pressures in the reaction enable synthesis gas to be introduced directly into the oxo plant and obviates the necessity to use high pressure compression equipment. This in turn reduces both capital costs and operating costs, as might be expected from the relative simplicity of the techniques employed. The catalyst is much easier to handle during operation.

The first three plants using the new technology are being built for Union Carbide Corporation itself. A 130,000 ton/year

plant for the production of *n*-butyraldehyde from propylene is under construction at the Ponce complex in Puerto Rico. Two units with a capacity of 45,000 ton/year for the production of propionaldehyde from ethylene are under construction at Texas City. These new plants will come into operation during 1975.

The first external licensee of the new process is in Sweden. Berol Kemi of Stenungsund is to build an oxo plant based on the propylene-to-*n*-butyraldehyde conversion to go on stream by early 1978. This plant is to have a capacity of 100,000 ton/year of *n*-butyraldehyde. Other products to be manufactured in this plant include butanol, octanol and octanoic acid.

Davy Powergas Limited, a member of the Davy International Company, will participate in the construction of all these plants, and the rhodium-containing catalyst will be supplied by Johnson Matthey Chemicals Limited.

Intercrystalline Rupture of Platinum Alloys

GRAIN BOUNDARY MIGRATION AND INTERCRYSTALLINE SLIP NEAR WELDS

The fabrication of articles from platinum alloys generally requires the use of welding techniques but the difficulty sometimes arises that intercrystalline cracking occurs in the vicinity of the welded seam. The exact conditions under which this problem arises have yet to be fully defined. However, progress in this direction has been made by a team of workers at the Ural Polytechnic Institute named for S. M. Kirov (V. V. Stepanov, T. A. Chernyshova and V. V. Shevelev, *Fiz. Metal. Metalloved.*, 1975, **39**, (1), 183-188).

The alloys studied were 7 per cent rhodium-platinum, 10 per cent rhodium-platinum and 5 per cent rhodium-15 per cent palladium-platinum. Results were obtained for the effect of chemical composition on the tendency to crack formation and for the process of grain growth during repeated welding cycles.

A large number of welds and their surrounding zones were observed in all three alloys. These indicated that twice as much cracking occurred in the ternary alloy as in 7 per cent rhodium-platinum but that the least amount of cracking occurred in 10 per

cent rhodium-platinum. Small additions of magnesium, iron, calcium, aluminium, and silicon and of their combinations were made to the alloys. It was found that more cracking resulted, particularly induced by additions of silicon, aluminium and calcium.

Fractographic analysis was undertaken to establish the mechanism of cracking before attempting to eliminate it. Two features became apparent. First, lines of intercrystalline slippage develop and, secondly, secondary phases in the form of fine dark deposits occur on the facets and boundaries of the crystals. The latter incorporate the deleterious additions.

A suggested mechanism for crack formation is that voids form between crystals because of slip. The links between crystals are thus broken and cracking is initiated. To verify this mechanism grain growth was observed closely in the weld and in the surrounding area. The thermal effects of welding induce grain growth in the alloys and this in turn may cause the intercrystalline slip which leads to voids and rupture at certain temperatures of welding, especially for impure alloys.