



Aqueous phase catalytic hydroformylation reactions of alkenes



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ARTICLE INFO

Article history:

Received 29 March 2014

Received in revised form 23 June 2014

Accepted 30 July 2014

Available online 18 September 2014

Keywords:

Biphasic hydroformylation

Aqueous phase

Alkene

Aldehyde

Surfactant

Cyclodextrins

ABSTRACT

The present article provides an overview of the recent developments in the area of aqueous phase hydroformylation of alkenes. The commercial application of aqueous phase hydroformylation reaction is restricted to the lower carbon chain alkenes due to the solubility and mass transfer limitations of the higher carbon chain alkenes in aqueous phase. The approaches which have been developed to improve the solubility of higher carbon chain length alkenes for aqueous phase hydroformylation reaction are emphasized in this article.

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1. Introduction

Hydroformylation or oxo reaction is a commercially important reaction to produce aldehydes from the reaction of an alkene with syn-gas (mixture of hydrogen and carbon monoxide) in the presence of a catalyst (Scheme 1).

The primary products of a hydroformylation reaction are linear and branched aldehydes with an additional carbon atom added to the reactant alkene. The obtained aldehydes can be converted into other commercially important chemicals via subsequent reactions, like hydrogenation, condensation, amination, and oxidation. Generally, linear (*n*) aldehydes are more valuable than the branched (iso) aldehydes, therefore, the *n* to iso ratio of aldehydes and the rate of formation are important parameters to be considered in an industrial hydroformylation process. The alkene hydroformylation is an important reaction for C–C bond formation and functionalization of C–C bonds with diverse functional groups to produce fine chemicals [1–3]. The chiral compounds for the production of pharmacologically active molecules and agrochemicals can be synthesized by asymmetric hydroformylation with controlled enantio-, chemo- and regio-selectivity [4,5].

2. Commercial significance

World production and consumption of hydroformylation (oxo) chemicals is about 11 million metric tons per year with expected growth rate of 4.0% per year [6]. These oxo chemicals are used to produce solvents, detergents, plasticizers, fragrances and intermediates for fine and specialty chemical industry.

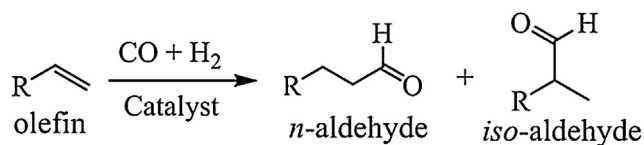
Propanal produced by ethylene hydroformylation and its derivatives is used as a solvent, pesticide intermediates and printing ink applications. Propanol is used as a precursor for glycol ether and surface coating applications. The other propanal derivatives, sodium and calcium propionates finds application in the grain and food preservatives, 3,4-dichloropropionanilide as a herbicide and cellulose acetate propionate, as a plastic sheeting and molding precursor.

The market demand for C₄ aldehydes which are synthesized by hydroformylation of propylene is higher among all oxo chemicals due to its consumption for the production of 2-ethylhexanol and butanol. 2-Ethylhexanol is used for the production of dioctyl phthalate, other plasticizers, coatings, adhesives, stabilizers, perfumery and specialty chemicals. 2-Ethylhexanol derivatives are used as additives for diesel fuel to reduce emissions and for lube and mining oil to improve its performance. *n*-Butanol is used for the production of coating systems, cleaning fluids, herbicides, dyes, printing inks, personal care products, pharmaceuticals, plasticizers, textiles and lube additives.

Among C₅ aldehydes, *n*-pentanal (valeraldehyde) is the fastest growing oxo chemical, used for production of 2-propylheptanol. Valeraldehyde derivatives are used predominantly to make lube oil

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Scheme 1. Hydroformylation reaction.

additives, which find application especially in automotive sector. *n*-Valeric acid, which is prepared by hydroformylation of butene followed by subsequent oxidation, is the basis of new ester type lubricants for CFC-substitution in refrigeration systems. Volatile esters of valeric acid are used in perfumes and cosmetics due to their pleasant odor. The ethyl valerate and pentyl valerate are used in food industries due to their fruity flavors.

C_6 – C_{13} aldehydes are consumed for the production of fine and perfumery chemicals, C_6 – C_{13} alcohols for the synthesis of plasticizers. C_{7-9} oxo acids which are the main derivatives of C_{7-9} oxo aldehydes are used mainly to produce neopolyol esters. The 1-heptanal which is produced by hydroformylation of 1-hexene is a perfumery chemical and is also used for the production of lubricants.

Linear C_{12} – C_{18} aldehydes find their applications in the detergent industries to synthesize detergent grade alcohols. The detergent grade alcohols can be converted into alcohol sulfates, ethoxylates, alcohol ether sulfates and fatty amines for the diverse applications.

3. Why aqueous phase hydroformylation

Typically, homogeneous catalysts comprising a transition metal and a ligand have been used for the hydroformylation of alkenes. These transition metal complexes interact with carbon monoxide (CO) and hydrogen (H_2) to form catalytically active metal carbonyl hydride species. The first generation of the hydroformylation catalyst was exclusively based on the cobalt metal (Fig. 1). The separation of products from reaction mixture, lower catalyst activity, higher reaction temperature and pressure are the major limitations of the first generation processes.

The second generation of the hydroformylation processes combined developments for ligand modification and replacement of the cobalt metal by rhodium. The rhodium metal modified by triphenylphosphine (PPh_3) ligand is termed as Low Pressure Oxo (LPO) process [7]. The selectivity and *n*/*iso* ratio of aldehydes improved significantly with highly active and selective homogeneous rhodium based complexes in LPO process. However, practical problems of separation of products from the reaction mixture, catalyst recovery and loss of expensive rhodium metal due to the lower thermal stability of the rhodium based complexes continued in the second generation catalysts too. In the hydroformylation process, leaching of rhodium metal has significant impact on the process economy. For example, leaching of 1 ppm rhodium per kg of product from a 400 kTA plant may result into the financial loss of several million euros [8]. These disadvantages inspired the development of a water soluble ligand, trisodium salt of tris(*m*-sulfonatophenyl)phosphine (TPPTS; $P(m-C_6H_4SO_3Na)_3$) in the third generation (1980s) hydroformylation catalyst

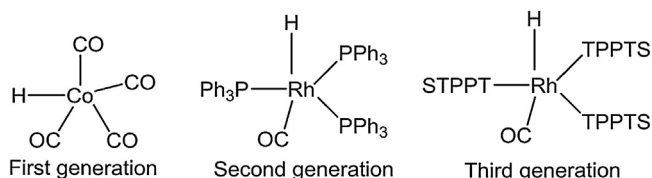
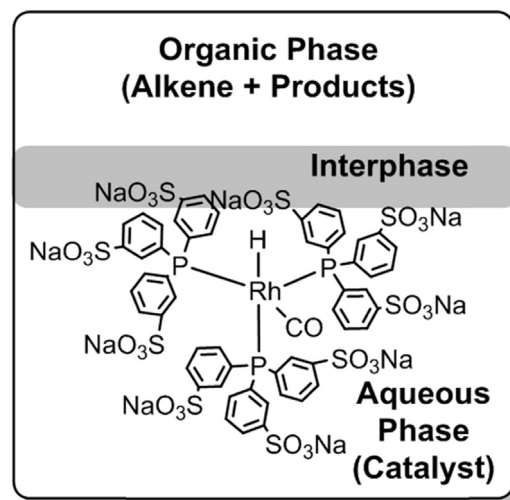


Fig. 1. Development of hydroformylation catalysts.

Fig. 2. Aqueous phase hydroformylation of alkene using $HRh(CO)(TPPTS)_3$ complex.

development [9–11]. The TPPTS ligand is highly soluble in water (c.a. 1.1 kg/L), mostly insoluble in common non-polar solvents and sufficiently stable under reaction conditions [12]. The rhodium complex of TPPTS ligand is a water soluble complex which can be separated easily from the reaction mixture after the completion of hydroformylation reaction in the aqueous phase. Despite all the limitations discussed above, all the three generations of hydroformylation processes are still in commercial operation. Besides, cobalt and rhodium metals, ruthenium, iridium, platinum, palladium and iron [13] have also been studied as alternative metals for hydroformylation, but poor activity of these metals compared to cobalt and rhodium has restricted their application for the commercial hydroformylation process.

In the aqueous phase hydroformylation reaction, the active catalyst for the reaction is dissolved in water and remains in the aqueous phase, whereas, reactants and products reside in the organic phase. The mixture of aqueous and organic phases forms two layers in the vessel and the reaction takes place at the interface as shown in Fig. 2. The separation of catalyst (water soluble) from the products mixture containing relatively non-polar organic compounds is carried out by simple decantation (phase separation). The aqueous phase containing the catalyst is recycled to the reactor and the organic phase is subjected for the purification of products. As compared to conventional homogeneous hydroformylation processes, further distillation is not required in the aqueous phase hydroformylation process to separate the catalyst from reaction mixture.

4. Commercial process for aqueous phase hydroformylation of propylene and butene

The water soluble rhodium complex based on the TPPTS ligand (1, Fig. 3) was commercialized in 1984 for the hydroformylation of propylene to produce C_4 aldehydes at Oberhausen site of Ruhrchemie AG (Ruhrchemie/Rhône-Poulenc (RCH/RP) process) [11,14–19]. This process works at milder reaction conditions (50 bar pressure and $120^\circ C$ temperature) to give 95% propylene conversion, 92–97% selectivity to the linear aldehyde with 99% selectivity of total C_4 aldehydes. The critical point in this process is the production of TPPTS as it is highly unstable in the presence of air/oxygen. In this process, TPPTS ligand is used around 50 fold in the excess to rhodium metal to achieve higher selectivity of *n*-aldehyde and to minimize rhodium leaching (less than 1 ppb rhodium leaching throughout catalyst batch life). The constant activity of catalyst can be maintained for several years by

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