

METAL-LIGAND COMPLEX CATALYZED PROCESSES

This application claims the benefit of provisional U.S. patent application Ser. Nos. 60/008284, 60/008286, 60/008289 and 60/008763, all filed Dec. 6, 1995, and all of which are incorporated herein by reference.

BRIEF SUMMARY OF THE INVENTION

1. Technical Field

This invention relates to an improved metal-organopolymorphosphite ligand complex catalyzed hydroformylation process directed to producing aldehydes. More particularly, this invention relates to conducting the hydroformylation process in a reaction region where the hydroformylation reaction rate is of a negative or inverse order in carbon monoxide which is sufficient to prevent and/or lessen deactivation of the metal-organopolymorphosphite ligand complex catalyst and at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process.

2. Background of the Invention

It is well known in the art that aldehydes may be readily produced by reacting an olefinically unsaturated compound with carbon monoxide and hydrogen in the presence of a rhodium-organophosphite ligand complex catalyst and that preferred processes involve continuous hydroformylation and recycling of the catalyst solution such as disclosed, for example, in U.S. Pat. Nos. 4,148,830; 4,717,775 and 4,769,498. Such aldehydes have a wide range of known utility and are useful, for example, as intermediates for hydrogenation to aliphatic alcohols, for aldol condensation to produce plasticizers, for oxidation to produce aliphatic acids, etc.

However, notwithstanding the benefits attendant with such rhodium-organophosphite ligand complex catalyzed hydroformylation processes, stabilization of the catalyst and organophosphite ligand remains a primary concern of the art. Obviously catalyst stability is a key issue in the employment of any catalyst. Loss of catalyst or catalytic activity due to undesirable reactions of the highly expensive rhodium catalysts can be detrimental to the production of the desired aldehyde. Likewise degradation of the organophosphite ligand employed during the hydroformylation process can lead to poisoning organophosphite compounds or inhibitors or acidic byproducts that can lower the catalytic activity of the rhodium catalyst. Moreover, production costs of the aldehyde product obviously increase when productivity of the catalyst decreases.

Numerous methods have been proposed to maintain catalyst and/or organophosphite ligand stability. For instance, U.S. Pat. No. 5,288,918 suggests employing a catalytic activity enhancing additive such as water and/or a weakly acidic compound; U.S. Pat. No. 5,364,950 suggests adding an epoxide to stabilize the organophosphite ligand; and U.S. Pat. No. 4,774,361 suggests carrying out the vaporization separation employed to recover the aldehyde product from the catalyst in the presence of an organic polymer containing polar functional groups selected from the class consisting of amide, ketone, carbamate, urea, and carbonate radicals in order to prevent and/or lessen rhodium precipitation from solution as rhodium metal or in the form of clusters of rhodium. Notwithstanding the value of the teachings of said

references, the search for alternative methods and hopefully an even better and more efficient means for stabilizing the rhodium catalyst and organophosphite ligand employed remains an ongoing activity in the art.

For instance, a major cause of organophosphite ligand degradation and catalyst deactivation of rhodium-organophosphite ligand complex catalyzed hydroformylation processes is due to the hydrolytic instability of the organophosphite ligands. All organophosphites are susceptible to hydrolysis in one degree or another, the rate of hydrolysis of organophosphites in general being dependent on the stereochemical nature of the organophosphite. In general, the bulkier the steric environment around the phosphorus atom, the slower the hydrolysis rate. For example, tertiary triorganophosphites such as triphenylphosphite are more susceptible to hydrolysis than diorganophosphites, such as disclosed in U.S. Pat. No. 4,737,588, and organopolymorphosphites such as disclosed in U.S. Pat. Nos. 4,748,261 and 4,769,498. Moreover, all such hydrolysis reactions invariably produce phosphorus acidic compounds which catalyze the hydrolysis reactions. For example, the hydrolysis of a tertiary organophosphite produces a phosphonic acid diester, which is hydrolyzable to a phosphonic acid monoester, which in turn is hydrolyzable to H_3PO_3 acid. Moreover, hydrolysis of the ancillary products of side reactions, such as between a phosphonic acid diester and the aldehyde or between certain organophosphite ligands and an aldehyde, can lead to production of undesirable strong aldehyde acids, e.g., $n-C_3H_7CH(OH)P(O)(OH)_2$.

Indeed even highly desirable sterically-hindered organobisphosphites which are not very hydrolyzable can react with the aldehyde product to form poisoning organophosphites, e.g., organomonophosphites, which are not only catalytic inhibitors, but far more susceptible to hydrolysis and the formation of such aldehyde acid byproducts, e.g., hydroxy alkyl phosphonic acids, as shown, for example, in U.S. Pat. Nos. 5,288,918 and 5,364,950. Further, the hydrolysis of organophosphite ligands may be considered as being autocatalytic in view of the production of such phosphorus acidic compounds, e.g., H_3PO_3 , aldehyde acids such as hydroxy alkyl phosphonic acids, H_3PO_4 and the like, and if left unchecked the catalyst system of the continuous liquid recycle hydroformylation process will become more and more acidic in time. Thus in time the eventual build-up of an unacceptable amount of such phosphorus acidic materials can cause the total destruction of the organophosphite present, thereby rendering the hydroformylation catalyst totally ineffective (deactivated) and the valuable rhodium metal susceptible to loss, e.g., due to precipitation and/or depositing on the walls of the reactor.

Compounding the organophosphite stability problem is the need to continually hydrolyze a poisoning or inhibiting organomonophosphite referred to above which forms during hydroformylation catalysis with a metal-organopolymorphosphite ligand complex catalyst. For example, if hydroformylation is operated under conventional conditions, a steadily declining catalyst activity is observed because of the accumulation of inhibiting organomonophosphite/organopolymorphosphite ligand-metal complexes. Attempts to prevent or lessen the accumulation of such organomonophosphite/organopolymorphosphite ligand-metal complexes can cause undesirable disruption of hydroformylation operating parameters, e.g., temperature, pressure, reaction rate, etc. Accordingly, a successful method for preventing and/or lessening the accumulation of such organomonophosphite/organopolymorphosphite ligand-metal complexes while at the same time minimizing disrupt-