

Description

Field of the invention

This invention concerns an improved process for carbonylating methanol to acetic acid.

Description of the prior art

Among currently-employed processes for synthesizing acetic acid one of the most useful commercially is the catalyzed carbonylation of methanol with carbon monoxide as taught in U.S. 3,769,329 issued to Paulik et al on October 30, 1973. The carbonylation catalyst comprises rhodium, either dissolved or otherwise dispersed in a liquid reaction medium or else supported on an inert solid, along with a halogen-containing catalyst promoter as exemplified by methyl iodide. The rhodium can be introduced into the reaction system in any of many forms, and it is not relevant, if indeed it is possible, to identify the exact nature of the rhodium moiety within the active catalyst complex. Likewise, the nature of the halide promoter is not critical. The patentees disclose a very large number of suitable promoters, most of which are organic iodides. These compounds are employed as promoters, not stabilizers. Most typically and usefully, the reaction is conducted with the catalyst being dissolved in a liquid reaction medium through which carbon monoxide gas is continuously bubbled.

Paulik et al teach that the liquid reaction medium can be any solvent compatible with the catalyst system and that it may comprise, for example, the pure alcohol which is being reacted, or mixtures thereof with the desired carboxylic acid end product and/or esters of these two compounds. However, the patentees teach further that the preferred solvent and liquid reaction medium for the process is the desired carboxylic acid itself, i.e., acetic acid when methanol is being carbonylated to produce acetic acid. Paulik et al also discloses that water may be added to the reaction mixture to exert a beneficial effect upon the reaction rate.

Considering specifically the carbonylation of methanol to acetic acid in a solvent comprising predominantly acetic acid and using the promoted catalyst taught by Paulik et al, it is taught in European Patent Application 0055 618 that about 14—15 wt% water is present in the reaction medium of a typical acetic acid plant using this technology. Recovering acetic acid in anhydrous or nearly anhydrous form from such a reaction solvent and separating the acetic acid from this appreciable quantity of water, involves substantial expenditure of energy in distillation and/or additional processing steps such as solvent extraction, as well as enlarging some of the process equipment as compared with that used in handling drier materials. Also Hjortkjaer and Jensen [Ind. Eng. Chem., Prod. Res. Dev. 16, 281—285 (1977)] have shown that increasing the water from 0 to 14 wt.% water increases the reaction rate of methanol carbonylation. Above that 14 wt.% water the reaction rate is unchanged.

Another disadvantage of the carbonylation process as just previously described is that the rhodium catalyst tends to precipitate out of the reaction medium, especially during the course of distillation operations to separate the product from the catalyst solution when the carbon monoxide content of the catalyst system is reduced (EP0055618). It has now been found that this tendency increases as the water content of the reaction medium is decreased. Thus, although it might appear obvious to try to operate the process of Paulik et al at minimal water concentration in order to reduce the cost of handling reaction product containing a substantial amount of water while still remaining enough water for adequate reaction rate, the requirement for appreciable water in order to maintain catalyst activity and stability works against this end.

Other reaction systems are known in the art in which an alcohol such as methanol or an ether such as dimethyl ether can be carbonylated or an acid or ester derivative using special solvents such as aryl esters of the acid under substantially anhydrous reaction conditions. The product acid itself can be a component of the solvent system. Such a process is disclosed in U.S. 4,212,989 issued July 15, 1980 to Isshiki et al, with the catalytic metal being a member of the group consisting of rhodium, palladium, iridium, platinum, ruthenium, osmium, cobalt, iron and nickel. A somewhat related patent in U.S. 4,336,399 to the same patentees, wherein a nickel-based catalyst system is employed. Considering U.S. 4,212,989 in particular, the relevance to the present invention is that the catalyst comprises both the catalytic metal, as exemplified by rhodium, along with what the patentees characterize as a promoter, such as the organic iodides employed by Paulik et al as well as what the patentees characterize as an organic accelerating agent. The accelerating agents include a wide range of organic compounds of trivalent nitrogen, phosphorus, arsenic, and antimony. Sufficient accelerator is used to form a stoichiometric coordination compound with the catalytic metal. Where the solvent consists solely of acetic acid, or acetic acid mixed with the feedstock methanol, only the catalyst promoter is employed (without the accelerating agent), and complete yield data are not set forth. It is stated, however, that in this instance "large quantities" of water and hydrogen iodide were found in the product, which was contrary to the intent of the patentees.

European Published Patent Application No. 0 055 618 to Monsanto Company discloses carbonylation of an alcohol using a catalyst comprising rhodium and an iodide or bromine component wherein precipitation of the catalyst during carbon monoxide-deficient conditions is alleviated by adding any of several named stabilizers. A substantial quantity of water, of the order of 14—15 wt.%, was employed in the reaction medium. The stabilizers tested included simple iodide salts, but the more effective stabilizers appeared to be any of several types of specially-selected organic compounds. When an iodide salt is used

as the stabilizer, the amount used is relatively small and the indication is that the primary criterion in selecting the concentration of iodide salt to be employed is the ratio of iodide to rhodium. That is, the patentees teach that it is generally preferred to have an excess of iodine over the amount of iodine which is present as a ligand with the rhodium component of the catalyst. Generally speaking the teaching of the patentees appears to be that iodide which is added as, for example, an iodide salt functions simply as a precursor component of the catalyst system. Where the patentees add hydrogen iodide, they regard it as a precursor of the promoter methyl iodide. There is no clear teaching that simple iodide ions as such are of any significance nor that it is desirable to have them present in substantial excess to increase the rate of the reaction. As a matter of fact Eby and Singleton [*Applied Industrial Catalysis*, Vol. 1, 275—296 (1983)] from Monsanto state that iodide salts of alkali metals are inactive as cocatalyst in the rhodium-catalyzed carbonylation of methanol.

Carbonylation of esters, such as methyl acetate, or ethers, such as dimethyl ether, to form a carboxylic acid anhydride such as acetic anhydride is disclosed in U.S. 4,115,444 to Rizkalla and in European Patent Application No. 0,008,396 by Erpenbach et al and assigned to Hoechst. In both cases the catalyst system comprises rhodium, an iodide, and a trivalent nitrogen or phosphorus compound. Acetic acid can be a component of the reaction solvent system, but it is not the reaction product. Minor amounts of water are indicated to be acceptable to the extent that water is found in the commercially-available forms of the reactants. However, essentially dry conditions are to be maintained in these reaction systems.

U.S. 4,374,070 to Larkins et al teaches the preparation of acetic anhydride in a reaction medium which is, of course, anhydrous by carbonylating methyl acetate in the presence of rhodium, lithium, and an iodide compound. The lithium can be added as lithium iodide compound. Aside from the fact that the reaction is a different one from that with which the present invention is concerned, there is no teaching that it is important per se that the lithium be present in any particular form such as the iodide. There is no teaching that iodide ions as such are significant. This patent further discloses feeding 2 to 7 volume % hydrogen to the reactor to suppress tar formation and significantly increase the reaction rate in terms of methyl acetate conversion as well as acetic anhydride production.

On the other hand, in an article in *Chem. Tech.*, Vol. 1, Oct. 1971, pages 600—605, James F. Roth et al describe the results of many experiments conducted on the carbonylation of methanol to acetic acid apparently utilizing the Monsanto commercial process. This process is essentially that described in previously mentioned U.S. 3,769,329 (Paulik et al). Among the results found was that the addition of hydrogen did not affect reaction rate. As hydrogen exerted no ill effect on the product composition, hydrogen was characterized as an inert diluent. Such finding is consistent with the disclosure in U.S. 3,769,329 wherein it is disclosed that carbon monoxide streams containing inert impurities such as hydrogen, carbon dioxide, methane, nitrogen, noble gases, water, and light paraffinic hydrocarbons may be employed from an available plant gas stream with no adverse effect, although in such cases total reactor pressure will have to be increased to maintain a desired carbon monoxide partial pressure. Concentrations of carbon monoxide in the feed gas mixture can be from 1 vol. percent to 100 vol. percent. Moreover, Paulik et al disclose that the rhodium-halogen catalyzed carbonylation process is readily adaptable to purifying hydrogen streams of carbon monoxide impurities since the carbon monoxide in such a gas mixture readily undergoes reaction with an alcohol, for example butyl alcohol to yield pentanoic acid.

Another patent describing the use of hydrogen in carbonylation reactions in U.K Patent Application GB 2155929, published October 2, 1985. In this particular patent, a process for producing acetic anhydride by the carbonylation of methyl acetate comprises separating the reaction mixture formed in the carbonylation reaction step into a volatile component and a rhodium-containing catalyst solution, heat treating the separated catalyst solution in the presence of a hydrogen-containing gas, and recirculating the hydrogenated catalyst solution to the carbonylation reaction step. It has been found that the activity of the rhodium catalyst was recovered. The patent specification states that the invention is also useful for the carbonylation of methanol.

In Japanese application 82-163034, Early Disclosure No. 60-53440, published March 28, 1985 is disclosed a process for simultaneously preparing acetic anhydride and acetic acid comprising carbonylating a mixture of methyl acetate and methanol in a liquid phase containing the presence of rhodium, a 3-substituted phosphine, chromium or zirconium, and an iodine compound. The carbon monoxide feed may contain 1 to 10 mol% H_2 to affect the selectivity of reaction and the life of catalytic activity. The molar ratio of methyl acetate to methanol in the mixture is disclosed as ranging from 1/3 to 3/1. A methyl acetate-methanol mixture containing an excessive amount of methanol used as feed is to be avoided since the amount of produced acetic anhydride is small and thus, would deviate from the object of the invention as well as to be troublesome to separate and obtain acetic anhydride from the reaction mixture. A methyl acetate-methanol mixture containing water, if in a small amount, is disclosed as being useful as the feed.

A similar process for the anhydrous co-production of acetic acid and acetic anhydride is disclosed in European Patent Application 170,965, published February 12, 1986 and assigned to Hoechst A. G. A catalyst system comprising rhodium and a phosphonium compound is used along with an organic iodide. Hydrogen can be added to the reaction medium in amounts of about 10 volume percent.

European patent applications 144,935 and 144,936, published June 19, 1985 and assigned to Union Carbide Corporation, disclose processes for the production of carboxylic acids from alcohols such as the

production of acetic acid from methanol. The two European patent applications disclose processes for the production of acetic acid by the catalytic reaction of methanol and carbon monoxide in contact with methyl acetate and a homogeneous catalyst system containing rhodium metal and lithium iodide, and rhodium metal and a mixture of lithium iodide and methyl iodide, respectively. Both of the published European patent applications state that the invention disclosed therein does not require the use of acidic halogen promoters as it employs the alkali metal halide lithium iodide, nor does the invention require the presence of water or use of large quantities of methyl iodide to give selectivity to acetic acid as taught in U.S. Patent No. 3,769,329 to Monsanto. Other than this broad statement, the published European patent applications to Union Carbide are silent on the effect of water on reaction rate.

An improvement in the prior-art process for the carbonylation of an alcohol to produce the carboxylic acid having one carbon atom more than the alcohol in the presence of a rhodium catalyst is disclosed in European Patent application 161,874; published November 21, 1985. As disclosed therein acetic acid (HOAc) is produced from methanol (MeOH) in a reaction medium comprising methyl acetate (MeOAc), methyl halide, especially methyl iodide, (MeI), and rhodium present in a catalytically-effective concentration. The invention therein resides primarily in the discovery that catalyst stability and the productivity of the carbonylation reactor can be maintained at surprisingly high levels, even at very low water concentrations, i.e. 4 wt.% or less, in the reaction medium (despite the general industrial practice of maintaining approximately 14 wt.% or 15 wt.% water) by maintaining in the reaction medium, along with a catalytically-effective amount of rhodium, at least a finite concentration of water, methyl acetate and methyl iodide, and a specified concentration of iodide ions over and above the iodide content which is present as methyl iodide or other organic iodide. The iodide ion is present as a simple salt, with lithium iodide being preferred. The application teaches that the concentration of methyl acetate and iodide salts are significant parameters in affecting the rate of carbonylation of methanol to produce acetic acid especially at low reactor water concentrations. By using relatively high concentrations of the methyl acetate and iodide salt, one obtains a surprising degree of catalyst stability and reactor productivity even when the liquid reaction medium contains water in concentrations as low as about 0.1 wt.%, so low that it can broadly be defined simply as "a finite concentration" of water. Furthermore, the reaction medium employed improves the stability of the rhodium catalyst, i.e. resistance to catalyst precipitation, especially during the product-recovery steps of the process wherein distillation for the purpose of recovering the acetic acid product tends to remove from the catalyst the carbon monoxide which in the environment maintained in the reaction vessel, is a ligand with stabilizing effect on the rhodium. EP-A-0161874 is herein incorporated by reference.

In summary, with exception to the improved carbonylation process as described in EP-A-0161874, current technology in the field of carbonylating an alcohol such as methanol to form a carboxylic acid such as acetic acid lacks a simple method for maintaining a highly stable catalyst system and for attaining industrially attractive conversion rates at conditions of low water content in the liquid reaction medium whereby the expense and capital investment costs of recovering the acid product with a very low water content can be minimized. Even with the improved carbonylation process as described in EP-A-0161874, there is still a need to increase reaction rates.

It is, accordingly, an object of the present invention to provide a reaction system with which an alcohol, as exemplified by methanol, can be carbonylated to a carboxylic acid derivative such as acetic acid at an increased carbonylation rate above that which is disclosed in commonly assigned U.S. Serial No. 699,525 using a liquid reaction medium having a lower water content than heretofore considered feasible. It is another object to provide a catalyst system which, regardless of the water content of the reaction medium, will be of improved stability, i.e., more resistant to precipitation of solid catalyst therefrom. It is also a related object to provide a catalyst system characterized by a substantial reduction in the undesired formation of by-product propionic acid and carbon dioxide as compared with high water systems used in the prior art. Other objects will be apparent from the following description.

Summary of the invention

Broadly, the invention is an improvement in the rhodium-catalyzed carbonylation of an alcohol to produce a carboxylic acid having one carbon atom more than the alcohol. In particular, the invention is directed to producing acetic acid by the carbonylation of methanol. It has now been discovered that the presence of hydrogen in the reaction medium for the rhodium-catalyzed carbonylation of alcohols to carboxylic acid has a beneficial effect on reaction rates. This effect is particularly found when the reaction medium contains very low water concentrations of below 14 wt.%.

In accordance with the present invention a saturated alcohol is converted to a carboxylic acid by reacting the alcohol in the liquid phase with carbon monoxide in the presence of a reaction medium comprising a rhodium catalyst, the ester of the alcohol being carbonylated with the acid product of the carbonylation reaction, a halide derivative of the hydrocarbon corresponding to the alcohol, especially the iodide, and an iodide ion which is present in amounts over and above the iodide which is present as the hydrocarbon halide, and where the water concentration is below 14 wt.% and where the reaction medium further contains hydrogen in an amount sufficient to provide a hydrogen partial pressure of at least 4.0 psi (27.58 kPa) in the reactor. The hydrogen is preferably provided in the reactor by cofeeding hydrogen with the carbon monoxide reactant.

Brief description of the drawings

Figures 1 and 2 graphically illustrate interactions among the several reaction medium components in an example which forms the basis of the present invention.

Description of the preferred embodiments

The following description is directed to the carbonylation of methanol to produce acetic acid. However, the technology is applicable to the carbonylation of higher homologues of methanol to form acids which are the higher homologues of acetic acid.

There are two criteria which need to be satisfied to maintain optimal performance of a reaction system for the rhodium-catalyst carbonylation of methanol to acetic acid. This is over and above the maintenance of a stable catalyst system from which the rhodium catalyst does not precipitate during the course of product recovery. First, it is desired to maintain a high productivity in the carbonylation reactor itself, as measured by the quantity of acetic acid formed per unit time per unit volume or weight of liquid reaction medium contained in the reactor. This might be termed "reactor productivity" or "reactor space-time yield". Here again the art as it presently exists recognizes the need to maintain reactor productivity although it has not taught the presently-described methods for attaining this end.

Second, the present process improvement contemplates the maintenance of optimal productivity, as measured by the ultimately-recovered concentrated acetic acid in the combined system including both the carbonylation reactor and the product recovery system. Although the details of the product recovery system are not directly relevant to the present disclosure, it will be recognized by anyone skilled in the art that water is an undesirable component of the crude acetic acid and that the more water there is in this stream the greater will be the operating costs and required capital investment in the product recovery-purification system. Thus, there is also a "system productivity" to be considered in addition to the "reaction productivity" with the "system productivity" depending upon the degree to which water is kept out of the residue of the crude product stream. The dryer this stream is, the higher will be the over-all system productivity so long as reaction productivity is maintained.

The present process improvement is directed at maintaining both an optimal reactor productivity and also an optimal over-all system productivity. Fundamentally, the current state of the art seems to be resigned to accepting a relatively high water content in the liquid reaction medium with a resulting undesirably high water content in the crude acetic acid initially recovered from the reaction and primary product recovery system.

As previously explained, the rate of the carbonylation reaction according to the present state of the art has been highly dependent on water concentration in the reaction medium as taught by U.S. 3,769,329; EP0055618; and Hjortkjaer and Jensen (1977). That is, as the water concentration is reduced below about 14-15 wt.% water, the rate of reaction declines. The catalyst also becomes more susceptible to inactivation and precipitation when it is present in process streams of low carbon monoxide partial pressures. It has now been discovered, however, that by utilizing a novel reaction medium increased acetic acid-production capacity can be achieved at water concentrations below about 14 wt.% (at water contents above about 14 wt.%, the reaction rate is not particularly dependent on water concentration).

For the purposes of this invention, the catalyst which is employed includes a rhodium component and a halogen promoter in which the halogen is either bromine or iodine. Generally, the rhodium component of the catalyst system of the present invention is believed to be present in the form of a coordination compound of rhodium with a halogen component providing at least one of the ligands of such coordination compound. In addition to the coordination of rhodium and halogen, it is also believed that carbon monoxide ligands form coordination compounds or complexes with rhodium.

The rhodium component of the catalyst system in the present invention may be provided by introducing into the reaction zone rhodium in the form of rhodium metal, rhodium salts and oxides, organic rhodium compounds, coordination compounds of rhodium, and the like.

The halogen promoting component of the catalyst system consists of a halogen compound comprising an organic halide. Thus, alkyl, aryl, and substituted alkyl or aryl halides can be used. Preferably, the halide promoter is present in the form of an alkyl halide in which the alkyl radical corresponds to the alkyl radical of the feed alcohol which is carbonylated. For example, in the carbonylation of methanol to acetic acid, the halide promoter will comprise methyl halide, and more preferably methyl iodide.

The liquid reaction medium employed may include any solvent compatible with the catalyst system and may include pure alcohols, or mixtures of the alcohol feedstock and/or the desired carboxylic acid and/or esters of these two compounds. The preferred solvent and liquid reaction medium for the process of this invention comprises the carboxylic acid product. Thus, in the carbonylation of methanol to acetic acid, the preferred solvent is acetic acid.

Water is also added to the reaction medium, but, at concentrations well below what has heretofore been thought practical for achieving sufficient reaction rates. It is known that in rhodium-catalyzed carbonylation reactions of the type set forth in this invention, the addition of water exerts a beneficial effect upon the reaction rate (U.S. Patent No. 3,769,329). Thus, commercial operations run at water concentrations of at least 14 wt.% (EP 0055618). Accordingly, it is quite unexpected that reaction rates substantially equal to and above reaction rates obtained with such high levels of water concentration can be achieved with water concentrations below 14 wt.% and as low as 0.1 wt.%. In accordance with the

present invention, the desired reaction rates are obtained even at low water concentrations by including in the reaction medium an ester which corresponds to the alcohol being carbonylated and the acid product of the carbonylation reaction and an additional iodide ion which is over and above the iodide which is present as a catalyst promoter such as methyl iodide or other organic iodide. Thus, in the carbonylation of methanol to acetic acid, the ester is methyl acetate and the additional iodide promoter is an iodide salt, with lithium iodide being preferred.

It has been found that under low water concentrations, methyl acetate and lithium iodide act as rate promoters only when relatively high concentrations of each of these components are present and that the promotion is higher when both of these components are present simultaneously. This has not been recognized in the prior art previous to disclosure of commonly assigned U.S. Serial No. 699,525. The concentration of lithium iodide used in the reaction medium of the present invention is believed to be quite high as compared with what little prior art there is dealing with the use of halide salts in reaction systems of this sort.

It has now also been discovered that reaction mediums having a methyl acetate concentration of greater than about 2 wt.%, lithium iodide is necessary not only to increase the reaction rate but also to stabilize the rhodium catalyst due to the deleterious effect of high methyl acetate concentrations on its stability, even at high water concentrations.

It has now been determined for the various reaction components that the amounts of water, iodide salt, methyl acetate, and methyl iodide as set forth in the following Table I, in which there is set forth both a broad range and a preferred, or optimal, range, are necessary for obtaining both catalyst stabilization and reaction rate enhancement. The "preferred" range is that which is preferred from the standpoint of optimal performance of the entire system including the primary product recovery system as explained hereinabove. It will be seen that the recommended concentrations are the same for both stabilization and also rate enhancement with one exception: the exception is that the "preferred" range for methyl acetate is 0.5—5 wt.% for catalyst stabilization whereas it is 2—5 wt.% for optimal rate enhancement. Broadly, of course, this means that in either case a range between 0.5 wt.% and 5 wt.% would be satisfactory, but that, depending upon whether it is catalyst stabilization or maximal rate enhancement that one aims to maximize in a given plant operating situation, the bottom end of the desired methyl acetate range is slightly higher when maximal rate enhancement is being sought.

TABLE I

	Stabilization		Rate enhancement	
	Broad wt. %	Preferred wt. %	Broad wt. %	Preferred wt. %
H ₂ O	0.1—20	1—4	0.1—20	1—4
Inorganic iodide (as LiI)	2—20	10—20	2—20	10—20
MeOAc	0.5—30	0.5—5	0.5—30	2—5
MeI	5—20	12—16	5—20	12—16
HOAc	Balance	Balance	Balance	Balance
Rh (ppm)	200—1000	300—600	200—1000	300—600

An important addition to the reaction medium and the subject matter of the present invention is a finite concentration of hydrogen. While the prior art was concerned that hydrogen impurities in the carbon monoxide feedstream may be detrimental and discovered otherwise, characterizing hydrogen as a mere inert diluent, it has now been found that when utilizing the reaction medium of the present invention wherein the water content is well below commercial practice, hydrogen in the reactor is not merely an inert gas, but actually improves the reaction rate for the production of carboxylic acid. To achieve the improved reaction rates for the formation of the desired carboxylic acid, the carbonylation reactor should contain a hydrogen partial pressure of at least 4 psi (27,58 kPa) at the reactor conditions of 150—250°C and 15 to 40 atmospheres total reaction pressure. Preferably, the hydrogen partial pressure will be at least 10 psi (68,95 kPa), more preferably, at least 20 psi (137,9 kPa) with even H₂ partial pressures as high as 40 psi (275,8 kPa) providing rate enhancement. Higher partial pressures of H₂ are also contemplated by the invention although H₂ partial pressures above 150 psi (1034 kPa) are not believed to substantially improve reaction rates. All pressures as herein stated refer to absolute pressure.

The hydrogen in the carbonylation reactor is provided by cofeeding small amounts of hydrogen with

the carbon monoxide feed. To achieve the desired hydrogen partial pressures in the carbonylation reactor, the requirements of hydrogen in the feed are quite small. For example, to maintain a partial pressure of hydrogen in the reactor of from 4 psi (27,58 kPa) to 40 psi (275,8 kPa) with normal venting of the inert reaction gases, such as carbon dioxide and nitrogen feed concentrations of hydrogen of between 0.3 mol% to 2.5 mol% are all that is required. Hydrogen feed concentrations of from 0.3 mol% to 10 mol% are useful to provide sufficient hydrogen in the reaction. Preferably from 1 mol% to 5 mol% H₂ in the feed stream provides desired reaction rate enhancement for forming the carboxylic acid product. It can readily be seen that controlling the venting of product gases which will include co-fed hydrogen as well as hydrogen formed during reaction can affect the hydrogen partial pressure in the reactor. It is preferred to control the hydrogen partial pressure by including hydrogen in the feed stream as opposed to merely reducing the steady state venting of product gases inasmuch as the steady state concentration of inert gaseous byproducts may build up in the reactor thus reducing the reactor carbon monoxide partial pressure to where the reaction becomes dependent on the reactor carbon monoxide partial pressure.

What has been found is that the addition of hydrogen to the carbonylation reactor yields increased rates in the production of the carboxylic acid and, thus, in the carbonylation of methanol to acetic acid, yields increased rates of production of the acetic acid compared to the carbonylation of methanol wherein higher levels of hydrogen are not expressly maintained. This is contrary to what has been recognized in the art in which hydrogen was characterized as an inert diluent only with no adverse effect on reaction rates. The difference found herein concerning the effect hydrogen has on reaction rates is believed to be the result of the use of reaction mediums which contain low amounts of water, that is water contents below 14 wt.%, and preferably between 1 and 4 wt.% of the reaction medium. Further, not only are the rates of production of acetic acid increased, the rate of carbon dioxide formation is drastically reduced by providing a hydrogen partial pressure in the carbonylation reactor of at least 4.0 psi (27,58 kPa) and, in particular, when the hydrogen partial pressure approaches to 20 psi (137,9 kPa).

It is believed that the increase in reaction rates, especially for the production of acetic acid, found by increasing the hydrogen partial pressure in the carbonylation reactor involves shifts in the Rh^I/Rh^{III} equilibrium involved in the water gas shift reaction:



Therefore, as the hydrogen partial pressure increases, the Rh^I/Rh^{III} ratio increases and consequently the carbonylation rate increases and the water gas shift reaction decreases as shown by the increased rates of acetic acid and the decreased carbon dioxide product formation.

Useful feedstocks which can be carbonylated according to the teachings of the present invention include alkanols containing 1—20 carbon atoms. Preferred feedstocks are alkanols containing 1—10 carbon atoms, and more preferred are alkanols of 1—5 carbon atoms. Methanol is the particularly preferred feed and is converted to acetic acid in accordance with the teachings of the present invention.

In accordance with the present invention, the carbonylation reaction may be carried out by intimately contacting the above defined feed alcohol, which is in the liquid phase, with gaseous carbon monoxide bubbled through a liquid reaction medium containing the rhodium catalyst, halogen-containing promoting component, alkyl ester, and additional soluble iodide salt promoter, at conditions of temperature and pressure suitable to form the carbonylation product. Thus, if the feed is methanol, the halogen-containing promoting component will comprise methyl iodide, the alkyl ester will comprise methyl acetate and the iodide salt will comprise any of several soluble iodide salts which are useful. It will be recognized that it is the concentration of iodide ion in this catalyst system that is important and not the cation associated with the iodide, and that at a given molar concentration of iodide the nature of the cation is not as significant as the effect of the iodide concentration. Any metal iodide salt, or any iodide salt of any organic cation, can be used provided that the salt is sufficiently soluble in the reaction medium to provide the desired level of the iodide. The iodide salt can be a quaternary salt of an organic cation or the iodide salt of an inorganic cation, preferably it is an iodide salt of a member of the group consisting of the metals of Group Ia and Group IIa of the periodic table as set forth in the "Handbook of Chemistry and Physics" published by CRC Press, Cleveland, Ohio, 1975—76 (56th edition). In particular, alkali metal iodides are useful, with lithium iodide being preferred.

The reaction temperature will be approximately 150—250°C, with the temperature range of 180—220°C being the preferred range. The carbon monoxide partial pressure in the reactor can vary widely but is typically 2—30 atmospheres, and preferably, 4—15 atmospheres. Because of the partial pressure of by-products and the vapor pressure of the contained liquids, the total reactor pressure will range from 15 to 40 atmospheres.

A reaction system which can be employed, within which the present improvement is used, comprises (a) a liquid-phase carbonylation reactor, (b) a so-called "flasher", and (c) a "methyl iodide-acetic acid splitter column". The carbonylation reactor is typically a stirred autoclave within which the reacting liquid contents are maintained automatically at a constant level. In this reactor there are continuously introduced fresh methanol, sufficient water to maintain at least a finite concentration of water in the reaction medium, recycled catalyst solution from the flash base, and recycled methyl iodide and methyl acetate from the overhead of the methyl iodide-acetic acid splitter column. Alternate distillation systems can be employed

so long as they provide means for recovering the crude acetic acid and recycling to the reactor catalyst solution, methyl iodide, and methyl acetate. In the preferred process, a mixed carbon monoxide/hydrogen feed is continuously introduced into the carbonylation reactor just below the agitator which is used to stir the contents. The mixed gaseous feed is, of course, thoroughly dispersed through the reactor liquid by this means. A gaseous purge stream is vented from the reactor to prevent buildup of gaseous by-products and to maintain a set carbon monoxide partial pressure at a given total reactor pressure. By controlling the venting of gases, it is also possible to control the hydrogen partial pressure in the reactor. The temperature of the reactor is controlled automatically, and the carbon monoxide/hydrogen feed is introduced at a rate sufficient to maintain the desired total reactor pressure.

Liquid product is drawn off from the carbonylation reactor at a rate sufficient to maintain a constant level therein and is introduced to the flasher at a point intermediate between the top and bottom thereof. In the flasher the catalyst solution is withdrawn as a base stream (predominantly acetic acid containing the rhodium and the iodide salt along with lesser quantities of methyl acetate, methyl iodide, and water), while the overhead of the flasher comprises largely the product acetic acid along with methyl iodide, methyl acetate, and water. A portion of the carbon monoxide and hydrogen along with gaseous by-products such as methane, hydrogen, and carbon dioxide exits the top of the flasher.

The product acetic acid drawn from the base of the methyl iodide-acetic acid splitter column (it can also be withdrawn as a side stream near the base) is then drawn off for final purification as desired by methods which are obvious to those skilled in the art and which are outside the scope of the present invention. The overhead from the methyl iodide-acetic acid splitter, comprising mainly methyl iodide and methyl acetate, is recycled to the carbonylation reactor along with fresh methyl iodide, the fresh methyl iodide being introduced at a rate sufficient to maintain in the carbonylation reactor the desired concentration of methyl iodide in the liquid reaction medium. The fresh methyl iodide is needed to compensate for losses of methyl iodide in the flasher and carbonylation reactor vent streams.

The primary reaction control method comprises continually analyzing the liquid contents of the reactor as well as the carbon monoxide and hydrogen content of the gas in the reactor vent and, on the basis of these analyses, controlling the flow of carbon monoxide, hydrogen, water, methanol, and methyl iodide to maintain the specified reaction medium composition. It should be further explained that the methanol addition to the carbonylation reactor is based not on an analysis of its contents for methanol but, rather, on analysis for methyl acetate content. Most of the methanol is converted almost immediately to methyl acetate when it enters the carbonylation reactor.

The process of the present invention may be operated either as a batch or as a continuous process. In batch operation the reactants are charged into the liquid catalyst solution, which is then subjected to the desired temperature and pressure conditions, after which the products are separated from the reaction mixture. In a continuous process which is described above, the catalyst system is maintained in liquid state, with the reactants being continuously supplied to the reaction zone containing the catalyst system at the desired temperature and pressure. The products are continuously withdrawn, as described above by withdrawing a portion of the solution containing the catalyst system, unreacted feed, equilibrium components, and the desired product. The desired product is then separated from such solution to permit recycling of the catalyst containing solution which includes unreacted feed and also equilibrium components.

Examples

Figures 1 and 2 correspond to Example 1 wherein the affect of hydrogen partial pressure on reaction rates and byproduct formation was evaluated.

The pilot plant was operated in the manner previously described in which there was included as a reactor a stirred autoclave followed by two product recovery system distillation steps. The process control scheme was as described also hereinabove. The reactor temperature in all cases was between 190°C and 195°C. The total reactor pressure was approximately 28 atmospheres, with the carbon monoxide partial pressure being approximately 8 to 12 atmospheres. In each case, the balance of the liquid reaction medium, not specifically listed in the corresponding figure was acetic acid. Because the reaction rate is directly proportional to the rhodium concentration, and to facilitate the comparison of the different runs, the STY in the runs set forth in the Figures have been normalized to 400 ppm rhodium unless otherwise indicated explicitly.

In the batch run, an autoclave of suitably corrosion-resistance metal was charged with rhodium triiodide (typically between 200 and 500 ppm rhodium content in the resulting mixture). The autoclave was sealed, pressured to approximately 28.2 atmospheres of carbon monoxide and the pressure checked at 25°C. After this the autoclave was slowly vented of its carbon monoxide content and then flushed two times by pressuring to 4.4 atmospheres with carbon monoxide followed by venting. The autoclave was then pressured to 11.2 atmospheres with carbon monoxide and heated to 185°C to 190°C, after which the agitator with which the autoclave was provided was turned on. The autoclave was then further pressured with carbon monoxide to 28.4 atmospheres. The rate of reaction was determined by monitoring the amount of carbon monoxide consumed over a period of time while assuming that the ideal-gas law applied to carbon monoxide. Reaction rate was determined from plots of carbon monoxide uptake versus time, the resulting data then being converted to the carbonylation reactor rate assuming ideal gas behaviour for the

carbon monoxide.

The glass vessel was actually composed of two side-by-side vessels fabricated from glass pipe and designed to operate at pressures not to exceed about 2 atmospheres gauge at 150°C. To conduct a run, each of the glass vessels was initially charged with the desired weight of rhodium (as salts like RhI_3), HI, acetic acid, water, and stabilizer. Both vessels were then pressurized to about 1.8 atmospheres gauge with carbon monoxide and heated in an oil bath to 130°C or 150°C in order to dissolve the rhodium. Carbon monoxide was then bubbled into the solution at 47 ml per minute through a gas-inlet tube while the desired constant pressure was maintained by a back-pressure regulator system. After one hour, the rhodium salt was completely dissolved in the form of a rhodium carbonyl compound. The carbon monoxide was replaced by nitrogen and the total pressure was reduced to 1 atmosphere gauge. This was considered the initial time of the stability experiment. Samples were removed through a sampling port, centrifuged for 5–10 minutes, and the clear centrifugate analyzed for soluble rhodium content.

Example 1

The effect of hydrogen partial pressure on reaction rates and byproduct formation was evaluated in a continuously-operating apparatus comprising a stirred reactor from which the product was drawn off continuously for a workup in the manner previously described. The reaction medium comprised 4 wt.% water, 3 wt.% methyl acetate, 12 wt.% methyl iodide, and 10–12 wt.% LiI. The reaction was run at 190°C and 400 psig pressure. Rhodium concentration varied between 335 ppm to about 800 ppm.

A base condition was run utilizing a pure carbon monoxide feed and three comparative runs containing 0.3 mol%, 1.3 mol% and 2.5 mol% hydrogen, respectively, in a mixed feed of CO and H_2 . The results are shown in Table II.

As can be seen, even at very low concentrations of hydrogen in the feedstream the production of acetic acid is increased and importantly, the production of carbon dioxide is greatly reduced. As the reactor hydrogen partial pressure is increased over the range of 1 psi to 40 psi, the reaction rate for the production of acetic acid is greatly increased and CO_2 production is reduced.

Figures 1, and 2 graphically illustrate what is set out in Table II for acetic acid production and CO_2 byproduct formation relative to the hydrogen partial pressure in the carbonylation reactor.

TABLE II*

H_2pp (psi)	HOAC STY (M/LHr)	CO_2 (%HOAC STY)	
3.3	10.4	0.26	100 mol% CO Feed
2.1	9.4	0.40	
2.1	9.3	0.41	
2.4	9.4	0.38	
2.9	9.6	0.40	
2.8	9.8	0.39	
1.6	9.4	0.39	
1.7	9.9	0.38	
1.6	10.0	0.33	
4.3	10.5	0.25	99.7 mol% CO+0.3 mol% H_2 Feed
6.7	10.0	0.26	
8.5	10.6	0.28	
8.1	10.5	0.25	
19.4	12.2	0.10	98.7 mol% CO+1.3 mol% H_2 Feed
21.3	13.1	0.08	
19.7	13.3	0.09	
20.8	11.9	0.16	97.5 mol% CO+2.5 mol% H_2 Feed
22.1	11.9	0.14	
38.7	12.8	0.08	
38.1	12.6	0.09	

* Reactor composition: 4 wt.% H_2O , 3 wt.% MeOAC, 12 wt.% MeI, 10 wt.%, LiI, 400 ppm Rh
Reactor conditions: 190 deg C, 28 atm Total Pressure

Claims

1. A process for producing a lower carboxylic acid by reacting a feed consisting essentially of an alcohol having one less carbon atom than said acid with carbon monoxide in a carbonylation reactor holding a liquid reaction medium containing a rhodium catalyst, the process comprising maintaining in said reaction medium during the course of said reaction quantity of water together with (a) a catalyst stabilizer selected from iodide salts which are soluble in said reaction medium at reaction temperature, (b) the iodide derivative of a lower hydrocarbon corresponding to said alcohol and (c) the ester of said alcohol with said carboxylic acid, characterised in that there is also maintained a partial pressure of hydrogen of at least 4 psi (27.58 kPa) at reaction conditions and the quantity of water is less than 14% by weight of said reaction medium.

2. The process of Claim 1 wherein said iodide salt is an iodide salt of a metal selected from Groups Ia and IIa or a quaternary iodide salt.

3. The process of Claim 2 wherein said iodide salt is lithium iodide salt.

4. The process of any of Claims 1—3 wherein said hydrogen is maintained at a partial pressure of at least 10 psi (68.95 kPa).

5. The process of Claim 4 wherein said hydrogen is maintained at a partial pressure of at least 20 psi (137.9 kPa).

6. The process of Claim 5 wherein said hydrogen is maintained at a partial pressure of at least 40 psi (275.8 kPa).

7. The process of any of Claims 1—6 where hydrogen is co-fed with said carbon monoxide in an amount of at least 0.3 mol% based on the carbon monoxide and hydrogen feed mixture to maintain said hydrogen partial pressure.

8. The process of Claim 7 wherein hydrogen is co-fed with said carbon monoxide in amounts of from 0.3 mol% to 10 mol% based on the carbon monoxide and hydrogen feed mixture to maintain said hydrogen partial pressure.

9. The improvement of Claim 8 wherein hydrogen is co-fed with said carbon monoxide in amounts of from 1 mol% to 5 mol% based on the carbon monoxide and hydrogen feed mixture to maintain said hydrogen partial pressure.

10. The process of any of Claims 1—9 wherein said water is present in amounts of between 1 and 4 wt.% of said reaction medium.

11. A process for producing acetic acid by reacting a feed consisting essentially of methanol with carbon monoxide in a carbonylation reactor holding a liquid reaction medium containing a rhodium catalyst, the process comprising maintaining catalyst stability and system productivity by maintaining in said reaction medium during the course of said reaction quantity of water together with (a) a catalyst stabilizer selected from iodide salts which are soluble in said reaction medium at reaction temperature, (b) methyl iodide, and (c) methyl acetate, characterized in that there is also maintained a partial pressure of hydrogen of at least 4 psi (27.58 kPa) at reaction conditions and the quantity of water is less than 14% by weight of said reaction medium.

12. The process of Claim 11 wherein said iodide salt is a quaternary iodide salt or an iodide salt of a member of the group consisting of the metals of Group Ia and Group IIa of the periodic table.

13. The process of Claim 12 wherein said iodide salt is an alkali metal iodide.

14. The process of Claim 13 wherein the iodide salt is lithium iodide.

15. The process of Claim 14 wherein the lithium iodide content is from 2 wt.% to 20 wt.%, the methyl acetate content is from 0.5 wt.% to 30 wt.%, and the methyl iodide content is from 5 wt.% to 20 wt.% with the balance consisting essentially of acetic acid, and wherein rhodium catalyst is maintained in said reaction medium in a concentration of 200 ppm to 1000 ppm calculated as rhodium.

16. The process of Claim 15 wherein, in weight percent, there is maintained in the reaction medium 1 to 4 wt.% water, 10 to 20 wt.% lithium iodide, 12 to 16 wt.% methyl iodide, and 0.5 to 5 wt.% methyl acetate when optimal catalyst stabilization is desired or 2 to 5 wt.% methyl acetate when maximal reactor productivity is desired, with the balance consisting essentially of acetic acid.

17. The process of any of Claims 11—16 wherein said hydrogen is maintained at a partial pressure of at least 10 psi (68.95 kPa).

18. The process of Claim 17 wherein said hydrogen is maintained at a partial pressure of at least 20 psi (137.9 kPa).

19. The process of Claim 18 wherein said hydrogen is maintained at a partial pressure of at least 40 psi (275.8 kPa).

20. The process of any of Claims 11—19 wherein hydrogen is co-fed with said carbon monoxide in an amount of at least 0.3 mol% based on the carbon monoxide and hydrogen feed mixture to maintain said hydrogen partial pressure.

21. The process of Claim 20 wherein hydrogen is co-fed with said carbon monoxide in amounts of from 0.3 mol% to 10 mol% based on the carbon monoxide and hydrogen feed mixture to maintain said hydrogen partial pressure.

22. The process of Claim 21 wherein hydrogen is co-fed with said carbon monoxide in amounts of from



1 mol% to 5 mol% based on the carbon monoxide and hydrogen feed mixture to maintain said hydrogen partial pressure.

Patentansprüche

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1. Verfahren zur Herstellung einer niederen Carbonsäure durch Umsetzen einer Beschickung, die hauptsächlich aus einem Alkohol, der ein Kohlenstoffatom weniger als die genannte Säure besitzt, besteht, mit Kohlenmonoxid in einem Carbonylierungsreaktor, in dem sich ein flüssiges, einen Rhodium-Katalysator enthaltendes Reaktionsmedium befindet, welches Verfahren die Aufrechterhaltung einer Wassermenge in dem genannten Reaktionsmedium während des Ablaufs der Reaktion in Verbindung mit (a) einem Katalysatorstabilisator in Form von in dem genannten Reaktionsmedium bei Reaktionstemperatur löslichen Iodidsalzen, (b) dem Jodidderivat eines dem genannten Alkohol entsprechend niederen Kohlenwasserstoffs und (c) dem Ester des genannten Alkohols mit der genannten Carbonsäure, umfaßt, dadurch gekennzeichnet, daß ferner ein Wasserstoffpartialdruck von mindestens 27,58 kPa (4 psi) unter Reaktionsbedingungen aufrechterhalten wird, und daß die Wassermenge weniger als 14 Gew.-% des genannten Reaktionsmediums beträgt.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Iodidsalz ein Iodidsalz eines Metalls aus der Gruppe Ia oder IIa oder ein quaternäres Iodidsalz ist.

3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß das genannte Iodidsalz Lithiumiodidsalz ist.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß der genannte Wasserstoff auf einem Partialdruck von mindestens 68,96 kPa (10 psi) gehalten wird.

5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß der genannte Wasserstoff auf einem Partialdruck von mindestens 137,9 kPa (20 psi) gehalten wird.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß der genannte Wasserstoff auf einem Partialdruck von mindestens 275,8 kPa (40 psi) gehalten wird.

7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß Wasserstoff zusammen mit dem genannten Kohlenmonoxid in einer Menge von mindestens 0,3 Mol-%, bezogen auf das Kohlenmonoxid- und Wasserstoff-Beschickungs-Gemisch, zugeführt wird, um den genannten Wasserstoff-Partialdruck aufrechtzuerhalten.

8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß Wasserstoff zusammen mit dem genannten Kohlenmonoxid in Mengen von 0,3 Mol-% bis 10 Mol-%, bezogen auf das Kohlenmonoxid- und Wasserstoff-Beschickungs-Gemisch, zugeführt wird, um den genannten Wasserstoff-Partialdruck aufrechtzuerhalten.

9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß Wasserstoff zusammen mit dem genannten Kohlenmonoxid in Mengen von 1 Mol-% bis 5 Mol-%, bezogen auf das Kohlenmonoxid- und Wasserstoff-Beschickungs-Gemisch, zugeführt wird, um den genannten Wasserstoff-Partialdruck aufrechtzuerhalten.

10. Verfahren nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß das genannte Wasser in Mengen von 1 bis 4 Gew.-% des genannten Reaktionsmediums vorliegt.

11. Verfahren zur Herstellung von Essigsäure durch Umsetzen einer Beschickung, die hauptsächlich aus Methanol besteht, mit Kohlenmonoxid in einem Carbonylierungsreaktor, in dem sich ein flüssiges, einen Rhodium-Katalysator enthaltendes Reaktionsmedium befindet, welches Verfahren die Aufrechterhaltung der Katalysatorstabilität und der Systemproduktivität durch Aufrechterhaltung einer Wassermenge in dem genannten Reaktionsmedium während des Ablaufs der Reaktion in Verbindung mit (a) einem Katalysatorstabilisator, ausgewählt unter in dem genannten Reaktionsmedium bei Reaktionstemperatur löslichen Iodidsalzen, (b) Methyljodid und (c) Methylacetat, umfaßt, dadurch gekennzeichnet, daß ferner ein Wasserstoff-Partialdruck von mindestens 27,58 kPa (4 psi) unter Reaktionsbedingungen aufrechterhalten wird, und daß die Wassermenge weniger als 14 Gew.-% des genannten Reaktionsmediums beträgt.

12. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß das genannte Iodidsalz ein quaternäres Iodidsalz oder ein Iodidsalz eines Elements der Gruppen Ia oder IIa des periodischen Systems der Elemente ist.

13. Verfahren nach Anspruch 12, dadurch gekennzeichnet, daß das genannte Iodidsalz ein Alkalimetalliodid ist.

14. Verfahren nach Anspruch 13, dadurch gekennzeichnet, daß das Iodidsalz Lithiumiodid ist.

15. Verfahren nach Anspruch 14, dadurch gekennzeichnet, daß der Lithiumiodid-Gehalt 2 Gew.-% bis 20 Gew.-% beträgt, der Methylacetat-Gehalt 0,5 Gew.-% bis 30 Gew.-% beträgt und der Methyljodid-Gehalt 5 Gew.-% bis 20 Gew.-% beträgt, wobei der Rest hauptsächlich aus Essigsäure besteht und wobei Rhodium-Katalysator in dem genannten Reaktionsmedium in einer Konzentration zwischen 200 ppm und 1000 ppm, berechnet als Rhodium, vorliegt.

16. Verfahren nach Anspruch 15, dadurch gekennzeichnet, daß in dem Reaktionsmedium 1 bis 4 Gew.-% Wasser, 10 bis 20 Gew.-% Lithiumiodid, 12 bis 16 Gew.-% Methyljodid und 0,5 bis 5 Gew.-% Methylacetat vorliegen, wenn optimale Katalysator-Stabilisierung angestrebt wird, oder 2 bis 5 Gew.-% Methylacetat, wenn maximale Reaktorproduktivität angestrebt wird, wobei der Rest im wesentlichen aus



Essigsäure besteht.

17. Verfahren nach einem der Ansprüche 11 bis 16, dadurch gekennzeichnet, daß der genannte Wasserstoff auf einem Partialdruck von mindestens 68,95 kPa (10 psi) gehalten wird.

18. Verfahren nach Anspruch 17, dadurch gekennzeichnet, daß der genannte Wasserstoff auf einem Partialdruck von mindestens 137,9 kPa (20 psi) gehalten wird.

19. Verfahren nach Anspruch 18, dadurch gekennzeichnet, daß der genannte Wasserstoff auf einem Partialdruck von mindestens 275,8 kPa (40 psi) gehalten wird.

20. Verfahren nach einem der Ansprüche 11 bis 19, dadurch gekennzeichnet, daß Wasserstoff zusammen mit dem genannten Kohlenmonoxid in einer Menge von mindestens 0,3 Mol-%, bezogen auf das Kohlenmonoxid- und Wasserstoff-Beschickungs-Gemisch, zugeführt wird, um den genannten Wasserstoff-Partialdruck aufrechtzuerhalten.

21. Verfahren nach Anspruch 20, dadurch gekennzeichnet, daß Wasserstoff zusammen mit dem genannten Kohlenmonoxid in Menge von 0,3 Mol-% bis 10 Mol-%, bezogen auf das Kohlenmonoxid- und Wasserstoff-Beschickungs-Gemisch, zugeführt wird, um den genannten Wasserstoff-Partialdruck aufrechtzuerhalten.

22. Verfahren nach Anspruch 21, dadurch gekennzeichnet, daß Wasserstoff zusammen mit dem genannten Kohlenmonoxid in Mengen von 1 Mol-% bis 5 Mol-%, bezogen auf das Kohlenmonoxid- und Wasserstoff-Beschickungs-Gemisch zugeführt wird, um den genannten Wasserstoff-Partialdruck aufrechtzuerhalten.

Revendications

1. Procédé de production d'un acide carboxylique inférieur, par réaction d'une alimentation consistant essentiellement en un alcool ayant un atome de carbone de moins que ledit acide avec de l'oxyde de carbone dans un réacteur de carbonylation retenant un milieu réactionnel liquide contenant un catalyseur de rhodium, le procédé comprenant le maintien dans ledit milieu réactionnel, pendant le cours de ladite réaction, d'une quantité d'eau avec (a) un stabilisant du catalyseur choisi parmi des sels d'iode qui sont solubles dans ledit milieu réactionnel à la température de réaction, (b) le dérivé d'iode d'un hydrocarbure inférieur correspondant audit alcool et (c) l'ester dudit alcool avec ledit acide carboxylique, caractérisé en ce que l'on maintient également une pression partielle d'hydrogène d'au moins 4 psi (27,58 kPa) aux conditions de réaction et que la quantité d'eau est plus faible que 14% en poids dudit milieu réactionnel.

2. Procédé de la revendication 1, où ledit sel d'iode est un sel d'iode d'un métal choisi dans les groupes Ia et IIa ou un sel d'iode quaternaire.

3. Procédé de la revendication 2, où ledit sel d'iode est un sel d'iode de lithium.

4. Procédé selon l'une quelconque des revendications 1—3, où ledit hydrogène est maintenu à une pression partielle d'au moins 10 psi (68,95 kPa).

5. Procédé de la revendication 4, où ledit hydrogène est maintenu à une pression partielle d'au moins 20 psi (137,9 kPa).

6. Procédé de la revendication 5, où ledit hydrogène est maintenu à une pression partielle d'au moins 40 psi (275,8 kPa).

7. Procédé selon l'une quelconque des revendications 1—6, où l'hydrogène est co-alimenté avec ledit oxyde de carbone en une quantité d'au moins 0,3 mole % en se basant sur le mélange d'alimentation d'hydrogène et d'oxyde de carbone pour maintenir ladite pression partielle d'hydrogène.

8. Procédé de la revendication 7, où l'hydrogène est co-introduit avec ledit oxyde de carbone en quantités de 0,3 mole % à 10 moles % en se basant sur le mélange d'alimentation d'hydrogène et d'oxyde de carbone pour maintenir ladite pression partielle d'hydrogène.

9. Perfectionnement de la revendication 8, où l'hydrogène est co-introduit avec ledit oxyde de carbone en quantités de 1 mole % à 5 moles % en se basant sur le mélange d'alimentation d'hydrogène et d'oxyde de carbone pour maintenir ladite pression partielle d'hydrogène.

10. Procédé selon l'une quelconque des revendications 1—9, où ladite eau est présente en quantité comprises entre 1 et 4% en poids dudit milieu réactionnel.

11. Procédé de production d'acide acétique par réaction d'une alimentation consistant essentiellement en méthanol avec de l'oxyde de carbone dans un réacteur de carbonylation retenant un milieu réactionnel liquide contenant un catalyseur de rhodium, le procédé consistant à maintenir la stabilité du catalyseur et la productivité du système en maintenant dans ledit milieu réactionnel, pendant le cours de ladite réaction, une quantité d'eau avec (a) un stabilisant du catalyseur choisi parmi des sels d'iode qui sont solubles dans ledit milieu réactionnel à la température de réaction (b) de l'iode de méthyle, et (c) de l'acétate de méthyle, caractérisé en ce que l'on maintient également une pression partielle d'hydrogène d'au moins 4 psi (27,58 kPa) aux conditions de réaction et que la quantité d'eau est inférieure à 14% en poids dudit milieu réactionnel.

12. Procédé de la revendication 11, où ledit sel d'iode est un sel d'iode quaternaire ou un sel d'iode d'un élément du groupe consistant en métaux du groupe Ia et du groupe IIa de la table périodique.

13. Procédé de la revendication 12, où ledit sel d'iode est un iode d'un métal alcalin.

14. Procédé de la revendication 13, où ledit sel d'iode est de l'iode de lithium.

15. Procédé selon la revendication 14, où la teneur en iode de lithium est comprise entre 2% en poids



et 20% en poids, la teneur en acétate de méthyle est comprise entre 0,5% en poids et 30% en poids, et la teneur en iodure, de méthyle est comprise entre 5% en poids et 20% en poids, le reste consistant essentiellement en acide acétique, et en ce que le catalyseur de rhodium est maintenu dans ledit milieu réactionnel à une concentration de 200 ppm à 1000 ppm en calculant sous la forme de rhodium.

16. Procédé selon la revendication 15, où, en pourcentage pondéral, on maintient, dans le milieu réactionnel 1 à 4% en poids d'eau, 10 à 20% en poids d'iodure de lithium, 12 à 16% en poids d'iodure de méthyle et 0,5 à 5% en poids d'acétate de méthyle lorsque l'on souhaite une stabilisation optimale du catalyseur ou 2 à 5% en poids d'acétate de méthyle lorsque l'on souhaite une productivité maximale du réacteur, le reste consistant essentiellement en acide acétique.

17. Procédé selon l'une des revendications 11—16, où ledit hydrogène est maintenu à une pression partielle d'au moins 10 psi (68,95 kPa).

18. Procédé de la revendication 17, où ledit hydrogène est maintenu à une pression partielle d'au moins 20 psi (137,9 kPa).

19. Procédé de la revendication 18, où ledit hydrogène est maintenu à une pression partielle d'au moins 40 psi (275,8 kPa).

20. Procédé selon l'une quelconque des revendications 11—19, où l'hydrogène est co-fourni avec ledit oxyde de carbone en une quantité d'au moins 0,3 mole% en se basant sur le mélange d'alimentation d'hydrogène et d'oxyde de carbone pour maintenir ladite pression partielle d'hydrogène.

21. Procédé de la revendication 20, où l'hydrogène est co-fourni avec ledit oxyde de carbone en quantités de 0,3 mole% à 10 moles% en se basant sur le mélange d'alimentation d'hydrogène et d'oxyde de carbone pour maintenir ladite pression partielle d'hydrogène.

22. Procédé de la revendication 21, où l'hydrogène est co-introduit avec ledit oxyde de carbone en quantités de 1 mole à 5 moles% en se basant sur le mélange d'alimentation hydrogène et d'oxyde de carbone pour maintenir ladite pression partielle d'hydrogène.

